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PROCEEDINGS

of the

NAPAP WORKSHOP ON DRY DEPOSITION

March 25-27, 1986
Harpers Ferry, West Virginia

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FOREWORD

The National Acid Precipitation Assessment Program was created in response to the perception of a problem: acid rain was seen to be damaging the environment. NAPAP is now six years old, with only four years left in which to resolve many remaining questions. Some of these questions have arisen as the result of research initiated under NAPAP, but others are carry-overs from earlier times, which NAPAP has so far not resolved. Until satisfactory answers are obtained to such questions, there will not be unanimity concerning the need for imposing new controls on emissions. It must be recognized that answers to all questions will not be obtained; instead, we must focus our limited energies and resources on questions to which answers are most urgently needed.

Existing abilities to study the effects of acid deposition (and to extrapolate from study locations where effects are carefully assessed) are limited by the uncertainty concerning the dry deposition component. This uncertainty affects modeling programs just as greatly. In particular, the tool that will be used to test the consequences of alternative control strategies is a numerical model, in which dry deposition is presently described with considerable uncertainty.

Dry deposition is known to approximate wet deposition of sulfur species, on the average, but it is also known that in some locations dry deposition can greatly exceed wet, and vice versa. The uncertainty regarding dry deposition is therefore viewed as a dominant problem confronting NAPAP in its final years. A key to all of the problems is the credibility of field measurements of dry deposition, from which all assessments of impacts are derived and on the basis of which all model parameterizations are developed. The workshop that generated these proceedings was seen as a first step towards addressing the question of technique credibility. A large number of informed scientists donated their time and effort to a three-day intensive debate on the present capabilities to quantify dry deposition, with special attention to the uncertainties and limitations of each method. The meeting was organized by the U. S. Department of Energy.

The gathering was asked to give special attention to the possibility that new measurement methods might exist, by application of which quick answers to key questions might now be obtained if some programmatic redirection were imposed or if new support were forthcoming. Inspection of the conclusions reveals support for the opinions widely voiced before the meeting: there is no new discovery that will provide an unequivocal answer within the near future. However several methods have been improved greatly in recent years. In general, it seems that the optimal path to success is to continue along the lines of current work, but with increased attention to several areas that are poorly addressed and with some new work to explore details of techniques of special promise.

PREFACE

That you are reading this report is clear evidence that you are interested in the issue of how to measure dry deposition and rather good evidence that you recognize the scientific complexity of this issue. I will, therefore, resist the ministerial temptation to lecture the choir and be content with outlining a very few thoughts.

The Department of Energy, sponsor of this Workshop, views atmospheric cleansing processes, both wet as well as dry, as fundamental concomitants of air pollution studies. As such, it has maintained a program of basic and applied research in these areas for two decades. The Department is gratified that the information and expertise it has developed has found application in NAPAP. It is certain that both the research and its application will be vigorous and useful activities for many years to come in contexts not yet part of the National scientific agenda.

David H. Slade, Director
Atmospheric Sciences Program/PTRD
Office of Health and Environmental Research
U.S. Department of Energy

DISCLAIMER

This document represents the conclusions of a scientific workshop on the subject of dry deposition. It has not been subjected to examination by any of the federal agencies or other organizations contributing to the workshop, and should not be interpreted as a statement of policy of any agency.

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I. EXECUTIVE SUMMARY

Understanding of air-surface dry exchange processes is vital in order to estimate amounts delivered to surfaces and to develop suitable, reliable methods to measure the deposition. The processes are complicated because types of substances of interest vary greatly in their physical and chemical form, and the chemical, physical, and biological properties of surfaces are extremely variable. Also, the interactions among surface components by means of aerodynamic modification of the efficiency of turbulent transport are poorly understood for the composites of surfaces that exist in nature. Additional research is needed to produce the knowledge necessary to determine atmospheric deposition to sensitive receptor areas.

In essence, knowledge of dry deposition is limited by the inability to make the necessary measurements in other than special circumstances. The need to generate confidence in the available measurement techniques was emphasized; in this regard there is need for more frequent collocation of experiments and for more collaboration of researchers. However, the discussions among the specialist groups focused attention on the greatly dissimilar experimental constraints associated with different techniques. A summary of relevant considerations is given in Table 1. Inspection of the tabulation indicates that extreme difficulties arise when trying to conduct a side-by-side comparison of all of the available methods. Moreover, in all cases there is need to improve measurement methods. This developmental effort is presently underway, but augmentation is required.

It is also evident that the present focus on questions regarding so-called acidic deposition is too confining to permit a broad-based attack on the overall problem of air pollution in the context of energy and agricultural options. In this regard, a program developed in response to questions concerning acidic deposition should not be expected to address questions arising in other contexts. However, the acid deposition concern is real and immediate, and if carefully arranged the research program generated to provide the most urgently desired answers could also constitute an entry into a longer-term investigation of broader issues.

A. Outstanding Deficiencies of the Existing Program

1. Chemical and Biological Factors

There is presently a lack of fundamental knowledge concerning the chemical and biological processes influencing dry deposition. Studies must be conducted to determine, for example, whether the transfers of NO, H_2O_2, etc., are influenced by stomatal resistance, and to explore the consequences of chemical reactions near the surface.

Methods must be developed to conduct laboratory and field investigations of the detailed pathways by which specific chemical species are deposited on surfaces, react with surfaces, or are absorbed by plant material.

Table 1. The applicability of related methods to specific experimental situations.

		Micrometeorology		Aircraft	Watersheds	Foliar Ext.	Inferential
	Surrogate Surfaces	Eddy Fluxes	Gradients	Eddy Fluxes		and Throughfall	
a: Terrain Complexity							
Flat, homogeneous	X	X	X	X	-	X	X
Flat, mixed surface	-	X	X	X	-	X	X
Rolling, homogeneous	-	X	-	X	X	X	X
Rolling, Mixed surface	-	X	-	X	X	X	X
Hills and valleys	-	-	-	X	X	X	-
Mountains	-	-	-	-	X	X	-
b: Chemical Species							
Sulfur dioxide	-	X	X	X	-	?	X
Ozone	-	X	X	X	-	-	X
Nitrogen dioxide	-	X	-	X	-	-	X
Nitric acid vapor	-	-	X	-	-	?	X
Particulate sulfate	-	X	X	-	-	X	X
Particulate nitrate	-	-	X	-	-	X	X
Particulate ammonium	-	-	X	-	-	-	X
Trace Metals	X	-	X	-	-	X	-
Submicron Particles	?	X	X	-	-	X	X
Supermicron Particles	X	-	-	-	-	X	
c: Time Scales							
Seconds	-	X	-	X	-	-	-
Minutes	-	X	-	X	-	-	-
Hours	X	X	X	X	-	X	X
Days	X	X	X	X	X	X	X
Months	-	-	X	-	X	X	X
Years	-	-	X	-	X	X	X
d: Spatial Scales							
10's of metres	X	X	X	-	-	X	X
100's of metres	-	X	X	X	X	X	X
1000's of metres	-	X	X	X	X	X	X
10's of km	-	-	-	X	-	-	-

The range of chemical species that can be investigated using micrometeorology must be increased. In particular, chemical sensors must be developed for use with eddy correlation and gradient methods.

Better methods must be developed for simple routine field measurements of concentrations of certain chemical species (especially HNO_3) for which the inferential "concentration monitoring" approach appears otherwise appropriate.

An improved conceptual approach is needed for monitoring dry deposition of several important species (such as NO, NH_3, and coarse particles) for which dry deposition cannot be easily computed from measurements of concentration monitoring data.

2. Scaling-up

Field measurements are inherently locally representative. At present, we understand the simplest situation the best.

It is not yet possible to extrapolate (with confidence) knowledge of the deposition behavior of uniform surfaces to a landscape matrix made up of these surfaces.

Dry deposition to complex terrain cannot be quantified, as yet, either by measurement or by models.

3. Scaling-down

Micrometeorological measurements address a surface that is constrained to be horizontally homogeneous. However, many studies are concerned with specific locations within the focal area.

The ability is lacking to relate (with confidence) the behavior of a complicated receptor surface to the behavior of its individual receptor elements.

B. General Recommendations

Two basic themes were common to the discussions of each of the four working groups, and were also explored in the final plenary session.

- Carefully-selected research sites should be identified to focus the attention of methods development and intercomparison studies on target regions of relevance to NAPAP programs. These sites would provide "benchmarks" for data derived elsewhere by the use of simpler, less direct methods.

- A program of controlled experiments should be initiated to test hypotheses associated with the measurement techniques now being developed, and to permit extension of experimental results to other situations and applications (e.g. numerical modeling).

Dry deposition research areas should be selected to be suitable for application of several measurement techniques. To assure that the

spectrum of methods is adequately covered, while also assuring that the facility is available to continue a logical (but accelerated) sequence of developmental steps, areas should provide access to a range of surface types:

- simple surface, simple terrain, for testing micrometeorological methods (including aircraft) and for evaluating methods for assessing dry deposition to a mosaic of surface vegetation,

- complicated surface, simple terrain, for developing the capability to determine area-wide average deposition over landscapes with a variety of species of vegetation,

- simple surface, typical terrain, for developing suitable experimental techniques,

- forested surface, simple terrain, (a) Coniferous; (b) Deciduous, and

- forested surface, typical terrain

  a. Coniferous; (i) Northern, (ii) Southern

  b. Deciduous; (i) Northern, (ii) Southern

It is anticipated that several of the needs may be satisfied at the same research area, provided sites are appropriately selected.

C. Controlled Experiments

Controlled experiments, supported by theoretical and modeling studies, are needed to test the utility of new measurement methods, and to develop techniques for extrapolating present understanding to other chemicals, biological species, geographic situations, and meteorological conditions. Several items were identified as being of special importance.

- Fundamental studies of deposition to non-biological surfaces should be conducted, to provide an improved understanding of the factors controlling transfer of both trace gases and particles in the immediate vicinity of receptor surfaces.

- Isotope studies of whole plants and of plant tissue are needed, to quantify biologically-controlled transfer rates and to investigate the roles of sulfur and nitrogen metabolization as it affects the extension of foliar extraction methods to gaseous sulfur and nitrogen species.

- Chamber studies in laboratory conditions are required, to expand the data base concerning knowledge of uptake according to biological species and chemical species.

- Field cuvette (and chamber) techniques should be used to test the extension of laboratory results to field conditions, and to

investigate the variations of stomatal resistance, cuticular resistance, etc., with height within plant canopies.

- The applicability of whole-plant foliar extraction methods should be explored further; such techniques could be used to extend throughfall methods (e.g., to new chemical species).

- An emphasis on sensor development is needed. New sensors are required to improve the detection of specific chemical constituents as required for exploitation of micrometeorological methods, for laboratory research, and for routine air concentration measurement programs.

- Turbulent flux measurement techniques require development, including the development and testing of aircraft eddy correlation methods but also including the improvement of methods to derive dry deposition fluxes from tower data. Candidate methods with special promise are identified earlier in this report.

The focus of these studies should be on the major issues identified previously; (a) to extend single-leaf results to whole-plant application, (b) to extend from whole-plants to uniform areas of the same species, (c) to derive area-averaged dry deposition from species-specific data obtained at single locations, (d) to describe deposition to a grid-cell area in terms of its component parts, and (e) to improve parameterizations in regional models.

II. INTRODUCTION

Dry deposition is one of the major mechanisms by which air pollutants can be delivered to sensitive surfaces, but measurement of dry deposition is difficult, especially on a long-term or routine basis.

Collection buckets fail to simulate the physical processes known to control the deposition of sub-micrometer particles to natural surfaces, and fail to give meaningful data on trace gas deposition, although some inert surfaces may provide useful data on the flux of coarse particles. The accumulation of depositing material on natural surfaces can be measured using established techniques, but the methods involved require further testing before routine application in dry deposition studies. For some chemical species, micrometeorological methods can be used to measure the flux to the surface, which can be equated to the surface deposition itself provided the field situation is adequate. In the lack of an existing method suitable for measurement of dry deposition on a routine basis, indirect methods are usually adopted. Knowledge of air concentrations alone is adequate for some purposes, such as for detecting trends with time at unchanging experimental sites, and hence a "concentration-monitoring" approach has gained favor. However, the link between air concentrations and dry deposition fluxes is not fixed, nor well known. The deposition velocity (defined as the ratio of dry deposition flux to air concentration at some reference height) can be specified for some chemical species and for some surfaces, and suggests the use of an approach by which dry deposition flux is computed from

air concentration data (either measured or modeled) using a value of the deposition velocity inferred from other information. Hence, there is a heirarchy of experimental methods, ranging in complexity from simple air concentration monitoring, through a variety of inferential methods, and extending to intensive micrometeorological and surface-sampling methods.

An understanding of air-surface dry exchange processes is vital in order to estimate amounts delivered from the air to surface and to develop suitable, reliable methods to measure the deposition. The processes are complicated firstly because types of substances of interest vary greatly in their physical and chemical form, and the chemical, physical, and biological properties of surfaces are extremely variable. Also, the interactions among surface components (by means of aerodynamic modification of the efficiency of turbulent transport) are poorly understood for the composites of surfaces that exist in nature.

It is generally conceded that existing methods for estimating dry deposition to sensitive receptor areas are quite deficient, and that an expanded research program is needed to improve these estimates. One of the goals of this workshop was to help guide decisions about how best to augment existing research efforts, to reduce existing uncertainties in both field measurements of dry deposition and in model computations.

Although there have been many rapid advances in related studies, the results of many of these investigations are slow in being applied. An initial workshop to examine methods of measurement of dry deposition was conducted at Argonne National Laboratory in 1979*. Many advances have been made in the subsequent seven years, while the importance of dry deposition has become increasingly apparent. For example, several surface analysis methods have been developed and applied in field studies since the 1979 workshop. Micrometeorological methods have been improved, and several new approaches to the problem of modeling dry deposition have been developed. In many cases, sufficient significant progress has been made that there is need to update the conclusions of the 1979 workshop.

Much of the present concern, regarding the modeling and measurement of dry deposition, results from activities on effects and long-range transport conducted as part of the National Acid Precipitation Assessment Program (NAPAP). At the request of the Director of Research of NAPAP (Dr. J. L. Kulp), a meeting was held at Harpers Ferry, West Virginia, on 25 - 27 March 1986, to review and "revisit" the conclusions of the 1979 workshop. A major goal of the 1986 workshop was to address the subject of technique uncertainty; specifically to explore ways in which uncertainty can be reduced by comparing widely different methods in selected circumstances.

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*Hicks, B. B., M. L. Wesely, and J. L. Durham, 1980: Critique of methods to measure dry deposition, workshop summary. EPA-600/9-80-050 and available as NTIS PB81-126443.

This report summarizes the deliberations and conclusions of the workshop. In the following sections, a state-of-the-science review of dry deposition is followed by the detailed reports of four working groups, addressing controlled experiments and associated modeling (B. B. Hicks, Chairman), surface analysis methods (S. E. Lindberg, Chairman), atmospheric flux methods (M. L. Wesely, Chairman), and siting strategies (S. M. Bromberg, Chairman). The reports of these four groups constitute the body of this document, and present alternative and complementary approaches to meeting NAPAP needs for dry deposition information.

A. List of Acronyms

AES	The Atmospheric Environment Service of Canada
ASRL	The Atmospheric Sciences Research Laboratory of EPA
ADOM	The Acid Deposition and Oxidant Model
CORE	The Core Research Establishments of the NOAA/EPA/DOE demonstration dry deposition measurement network.
DOE	The U. S. Department of Energy
EPA	The U. S. Environmental Protection Agency
NAPAP	The National Acid Precipitation Assessment Program
NCAR	The National Center for Atmospheric Research
NADP	The National Atmospheric Deposition Program
NOAA	The U. S. National Oceanic and Atmospheric Administration
NTN	The National Trends Network of NAPAP
PAN	Peroxyacetyl Nitrate
RADM	The Regional Acidic Deposition Model
SF	Stem flow
TF	Throughfall
VOC	Volatile Organic Compounds
WATOX	The Western Atlantic Ocean Experiment

III. BACKGROUND

Dry deposition is conveniently defined as the aerodynamic transfer of trace gases and aerosol from the air to the surface, and the gravitational settling of particles. Dry deposition is a subset of a larger group of processes identified as atmosphere/surface exchange.

Dry deposition data are needed for two basic reasons:

1) To specify the rate at which the atmosphere is being depleted.

2) To determine the rate of delivery of materials to the underlying surface.

In both contexts, there are needs for information to support both measurement and modeling programs. Some of these requirements demand fine time resolution of observations (or predictions) at specific locations, but others are satisfied by less intensive observing programs at a wider variety of locations.

A. Needs for Dry Deposition Information

1. For Assessment of Effects

Gaseous species are potentially more toxic to plants than particles because they can enter the leaves directly through open stomata and affect biochemical reactions and systems within the leaf. Particular concern is associated with sulfur dioxide, nitrogen oxides (and their products), and oxidants. Chemicals deposited as particles can enter the leaves more slowly, if they are water soluble, primarily by diffusion through the cuticle. Both gaseous and particulate materials may enter foliage indirectly by deposition to the soil, solubilization in soil water, movement through the roots and hence into the leaves.

A similar range of chemical species is of concern in the context of effects on aquatic systems, although oxidants are of lesser direct importance and particulate deposition may be more important. Effects on water quality and on aquatic biota generally require independent consideration. Stress upon biota may be indirect, in the sense that biological effects may be the result of chemical insults caused by increased levels of some intermediate chemical species, released as a consequence of atmospheric deposition. In general, it is the net consequence of deposition to entire catchment areas which is of concern, rather than the deposition to the water surface alone. In this context, it is important to recognize that water bodies usually have enriched surface films, which can affect exchange with the atmosphere and in concept could influence aquatic biology near the surface.

Sulfur dioxide and nitric acid vapor are perceived to be the most important trace gases causing damage on buildings and monuments. Oxidants are known to have a direct influence on organic surfaces, and could have less direct effects on other surfaces. Organic acids may also contribute to damage. As well as soiling the surface, deposited particles influence the ability of a material surface to capture other pollutants from the air. Moreover, trace metals, sulfate, nitrate, elemental carbon, etc., carried by particles can have adverse effects, undergoing a complicated series of reactions with substrate materials (and depositing gases) once deposited. Thus, in the case of effects on building materials, particles are potentially of greater importance than in the case of effects on other environmental systems. These effects potentially represent a substantial economic and aesthetic consequence of acid deposition. Estimates of deposition are required to quantify these consequences.

2. For Use in Models

Dry deposition of trace species can strongly influence concentration patterns and far downwind wet deposition of several trace gases and particles. According to several estimates, dry deposition of acidic sulfur and nitrogen is responsible for a significant fraction of total acidic deposition over the eastern United States. Additionally, dry deposition of several non-acidic trace gases (H_2O_2, O_3, NH_3, organics) can indirectly influence subsequent chemical interactions in the atmosphere, (which will in turn influence downwind wet and dry acid deposition), and can give rise to acidic species in soils after they are deposited. The link between emissions and deposition is being

addressed by Eulerian models, produced by combining detailed descriptions of all of the processes involved. Such regional-scale models of pollutant transport, transformation and deposition must adequately treat dry deposition of several trace species. Current regional acid deposition models compute deposition fluxes using parameterizations based on a relatively sparse database of SO_2, SO_4, HNO_3, NO_x (NO and NO_2) and O_3 dry deposition measurements. Unfortunately, for gases such as H_2O_2, PAN, NH_3, and other organic species, measurements that allow general deposition behavior to be understood have not been performed. Further studies of dry deposition are necessary to improve and evaluate the existing parameterizations of trace species dry deposition in regional-scale models, and to develop new formulations.

There are different requirements for dry deposition data for different pollutants, depending on the applications and on the models that are used. For example, from forest- and aquatic-effects viewpoints, there is relatively little need for data on the dry deposition of sub-micrometer particles (since they normally result in little dry deposition of acidic species to forests and aquatic ecosystems) whereas it is exactly these particles that are of great importance for studies of human health (since these particles can penetrate deep into lungs), visibility (these particles dominate atmospheric visibility reduction), and for long-range-transport modeling (since these particles can travel for long distances -- because of their small rate of dry deposition -- and then rapidly deposit in precipitation). For ecosystem-level-effects research, there is similarly relatively little interest in the dry deposition of a wide range of organic species (alkanes, alkenes, aromatics, aldehydes, etc.), but this information is needed for the atmospheric-chemistry modules of long-range-transport models, since these species can influence the production of $SO_4^=$ and NO_3^- within the atmosphere and in surface waters. Currently, the Regional Acidic Deposition Model (RADM: the Eulerian model presently under development for NAPAP by the National Center for Atmospheric Research) considers more than twenty different chemicals whose dry deposition must be specified.

Deposition flux is commonly expressed as the product of the atmospheric concentration of the chemical species under consideration at some convenient reference height and an appropriate deposition velocity. The deposition velocity can be characterized in terms of known properties, including such details as genotype-specific biological factors (e.g. stomatal resistance), and such data can be utilized in detailed numerical models that are tailored to the application. Some analytical procedures consider several layers within the canopy, but most represent the canopy as a net sink described in terms of some integrated stomatal resistance, cuticular resistance, soil resistance, etc.

An effort has been under way for several years to measure dry deposition by micrometeorological techniques, and to parameterize the results for use in Eulerian models. A large number of physical, chemical, and biological variables are taken into account and are

expressed in terms of resistances to vertical transport. Because of the simplifications necessary for use in regional atmospheric numerical models, surface resistances are generalized and are not highly site-specific. The chemical species include SO_2, NO, NO_2, HNO_3, O_3, and fine particulate sulfate and nitrate. The dry deposition modules of both RADM and the Acid Deposition and Oxidant Model (ADOM: developed under Canadian and German sponsorship) follows this approach.

Much of the work on the RADM dry deposition module has been conducted in association with investigations addressing needs of trial routine measurement programs. Many of the experiments have been conducted at the CORE research sites (see later). Although the data bases are similar for the two applications (routine measurement and modeling), it should be recognized that there are basic differences in the approaches. For use in regional source-receptor models, deposition velocity information for relatively large areas (20 km x 20 km) is required, and hence categorization of the surface according to land use has become popular. In the modeling application, it is also required that the deposition module make use of the "data" outputs of the main model in computing the deposition velocities. In contrast, the data analysis routines developed in support of routine measurement programs can be tailored to make use of field measurements of the most critical variables, at locations selected to be regionally representative.

B. Relative Importance of Chemical Species

The following discussion summarizes the importance of various gaseous and particulate pollutants, in the context of dry deposition. In this regard, it is clear that knowledge of the deposition flux is not always necessary -- present knowledge is sometimes limited to empirical relationships between effects and exposure conditions (so-called dose-response relationships). Pollutants have been sorted into three groups, corresponding to species that have (i) high importance in the context of effects (i.e., for which effects are known to occur, at some level of certainty), (ii) intermediate importance (i.e., effects have been indicated, and the level of importance is anticipated to be great, but there is little certainty as yet), and (iii) low importance (i.e., effects are known to be of little importance, or effects are unknown and expected to be fairly unimportant). The listing is not meant to be exhaustive. For example, HCl is not considered, and volatile organic compounds are not considered in depth.

1. Gaseous Pollutants

(a) High priority

SO_2. Sulfur dioxide is emitted directly into the atmosphere and is often considered to be the major pollutant of concern to NAPAP. Dry deposition of SO_2 is considered a major sink (and perhaps the dominant sink) of this species. Uptake of SO_2 at both organic and inorganic surfaces can be a direct acidification mechanism. SO_2 is thought to be rapidly deposited to moist surfaces, including vegetation.

NO_x. Nitrogen oxides (NO and NO_2 together) are generated by combustion processes, but are also produced by natural biological activity; they are generally considered to be the second most important species of direct NAPAP concern. Neither gas is highly soluble in water. NO_2, but not NO, is highly reactive to substances present in the environment, e.g. biological materials, presumably as a one-electron oxidizing agent, although this mechanism is not established with certainty. Chamber studies as well as field measurements have indicated that NO_2 is readily deposited to foliage. Less definitive information is available for NO, but indications are that deposition velocity of this species is much less than that of NO_2, perhaps near zero. Moreover, NO_2 concentration generally exceeds that of NO. For these reasons NO_2 is assigned high priority. NO is assigned intermediate priority - a compromise between the high importance if the deposition velocity is large and the high probability that this velocity is extremely low.

O_3. Ozone occurs naturally in the troposphere, but is also formed as a product of reactions involving hydrocarbons and nitrogen oxides. This connection with nitrogen oxides alone would serve to establish a NAPAP concern. In general, photochemistry involving O_3 is a major source of free radicals that not only drive gas-phase oxidation of NO (to NO_2), NO_2 (to HNO_3), and SO_2 (to H_2SO_4) but also form H_2O_2 (and other peroxides), which are responsible for aqueous-phase oxidation of SO_2 in acidic conditions. Dry deposition is a major sink of O_3. Additionally, O_3 is probably the best studied air pollutant and the most important pollutant from a vegetation effects standpoint. All of these reasons place O_3 at high priority.

HNO_3. Nitric acid is the final product of atmospheric oxidation of nitrogen oxides. It is a strong acid, highly soluble in water. It is thought to be dry deposited at a rate governed by atmospheric transport, consistent with its high solubility in water and reactivity with other environmental surfaces. The strong acidity of HNO_3 as well as its role as a plant nutrient establish the high importance of characterizing its dry deposition.

H_2O_2. Hydrogen peroxide is a product of the atmospheric photochemical cycle and may be a phytotoxicant in its own right. However, the principle reason for current interest in H_2O_2 is as an oxidant of SO_2 in cloud water. Dry deposition is probably a major sink of H_2O_2 (perhaps one-third; other sinks: photolysis, reaction with OH; reaction with SO_2; wet deposition).

NH_3. Ammonia is often not considered a pollutant of major concern to NAPAP. Sources of NH_3 are principally biological: animal wastes, fertilizer, etc. The reason for interest in NH_3 in the NAPAP context is that it is the principle atmospheric base available to neutralize acids of NAPAP concern. Reaction of NH_3 with acidic aerosol results in gas-to-particle conversion that in turn affects the deposition and fate of NH_3 (and $SO_4^=$, NO_3^-, etc.,).

Additionally NH_3, as an available nitrogen species, is a nutrient for nitrogen-deficient ecosystems. Available evidence indicates that deposition velocities of NH_3 may be large, in view of the high solubility of NH_3 at acidic to neutral pH.

(b) Intermediate Priority

NO. See above

HCHO and RCHO. Aldehydes are important in gas-phase photochemistry as sources (by photolysis) of free radicals, and consequently accurate description of sinks is important to photochemical models. Aldehydes are relatively soluble in water, and perhaps also in cuticular tissues. Aldehydes photolyze rapidly in air and perhaps after deposition to sunlit surfaces.

HCOOH, CH_3COOH. Formic and acetic acids are organic acids that contribute, albeit secondarily, to precipitation acidity. Little is known about atmospheric concentration or dry deposition fluxes, although their high solubility (as anions) suggests the possibility of a high deposition velocity.

PAN. Peroxyacetyl nitrate is a sink for atmospheric NO_x. It is a known phytotoxicant, and is often found in concentrations similar to those of HNO_3. The availability of data from relevant dose-response studies, as well as desire to describe total nitrogen flux to ecosystems place this species in the intermediate category.

(c) Low Priority

C_2H_4. Ethylene is a plant hormone as well as an indicator of plant stress and a phytotoxic air pollutant. However, dry deposition may not be a major sink, and at any rate the NAPAP connection is tenuous.

CO. Carbon monoxide is a significant anthropogenic pollutant that plays a role in gas-phase photochemistry leading to sulfur and nitrogen oxidation, H_2O_2 formation, etc. CO is such a long-lived species that models of photochemistry need not treat its dry deposition. Moreover, no phytotoxicant properties have been identified at pertinent concentrations.

HF. Hydrogen fluoride is an acid and as well a phytotoxicant. However, it is a pollutant of only local importance associated with aluminum smelting, production of superphosphate, and a number of smaller industries (e.g., glass manufacture and brick kilns). Thus, it is not of major concern to NAPAP.

2. Particulate Pollutants

From the perspective of relative contribution to deposition fluxes, dry deposition of aerosol particles is generally considered to be less important than that of trace gases, although specific instances arise in which particle exchange is critically important. It is usual to

differentiate between sub-micrometer particles (transferred through the air primarily by turbulence) and super-micrometer particles (for which gravitational settling contributes to the overall deposition). Some of the many reasons for emphasis on particle dry deposition can be deduced from the following list.

- Super-micrometer aerosol particles can deliver a significant fraction of the nutrients (especially $PO_4^{=}$, K^{+}, Ca^{++}, and $SO_4^{=}$) for forest and aquatic ecosystems.

- Air pollutants can be adsorbed at the surface of atmospheric particles, which can subsequently be deposited, or alternatively can exhibit lower deposition velocities than for the unadsorbed gases.

- Deposition of some sub-micrometer trace elements (especially heavy metals such as Pb and Cd) can be toxic to the same ecosystems.

- Direct impaction of polluted (e.g., acidic) cloud droplets on forests, especially on trees at forest edges, may contribute substantially to tree damage.

- Surfaces of some materials (including vegetation) may be damaged by the deposition of particles that catalyze the oxidation of SO_2, subsequently leading to pitting of the material at the site of the catalytic particle.

- Sub-micrometer particles are transported through the atmosphere for long distances (because of their generally low deposition velocity, a function of particle size and surface characteristics) and hence can be of considerable importance in the context of long-range transport modeling.

C. The Present NAPAP Program

1. Measurement Programs

A multi-agency program on methods development is being conducted, intended to provide the capability to measure the deposition of chemical species for which dry deposition cannot readily be computed from air concentration data. These include (1) the interpretation of gradients, variances, and covariances using simplified micrometeorological approaches, (2) a small effort to improve surrogate-surface methods for measuring particle deposition, and (3) research on the development and applicability of foliar extraction and throughfall methods. A related program is focusing on the need to improve techniques for measuring concentrations in air.

The existing program is directed towards provision of routine dry deposition data, largely because of the way in which the Task Groups were initially arranged. A glance at the program will identify three distinct components, with three substantially different goals.

(a) The EPA routine monitoring program

An EPA-NAPAP program is being initiated to monitor air concentrations and other variables related to dry deposition at locations identified as requiring dry deposition data for modeling purposes (presently five sites, but planned to expand to at least thirty).

Weekly data are desired, initially to be obtained using "day/night" sampling. However, it appears likely that the equipment will be capable of operation over shorter time intervals as well, in order to test shorter-term predictions of models.

Goal: As a first step, to provide air concentration data for testing transport and deposition models, probably using twelve-hour time resolution.

Chemical focus: Species important in modeling --- SO_2, HNO_3, NO_2, H_2O_2, O_3, NH_3, volatile organic compounds (VOCs), PAN etc., plus fine particulate $SO_4^=$, NO_3^-, NH_4^+, etc. Coarse particles are not addressed.

Siting: Initial emphasis on the Northeast, at locations required for testing RADM and ADOM models.

(b) The NOAA trial program

A NOAA-NAPAP program is attempting to infer dry deposition at a more widely spread network of locations (six in operation since 1984, and now numbering ten), selected to be in regionally representative areas where appropriate deposition velocities can be estimated from field data using current capabilities. The measurements focus on SO_2, HNO_3, and particulate anions and cations as reported by the National Trends Network (NTN). Weekly averages of concentrations are measured, using simple filterpacks (initially), with supporting hourly meteorological and surface data for computing deposition velocities. The method relies on the ability to deduce appropriate deposition velocities provided measurements are made of controlling surface and atmospheric properties. The approach is known as the "inferential method," in order to differentiate it from the more conventional "concentration monitoring" approach, which focuses on air quality alone.

Goal: As a first step, to develop a routine method for providing dry deposition data paralleling the wet deposition data of NTN.

Chemical focus: The measurements will ultimately focus on fine-particulate anions and cations as reported by NTN, plus SO_2 and HNO_3. In general, these are species for which inferential methods are appropriate. Coarse particles are not yet being considered.

Siting: Regionally representative subset of NTN.

(c) DOE/NOAA/EPA "CORE" network

A DOE/NOAA/EPA-NAPAP network of "CORE" research stations is intended to provide the basis for the deposition velocity parameterizations to be used in the inferential routine operations, and also to provide "benchmark" verifications of routine methods. At the time of this meeting, this network is made up of only three stations.

All chemical, meteorological, and surface data are recorded hourly (or more frequently), augmented by routine application of more direct dry deposition measurement methods (e.g., eddy correlation for one week every month) to provide the desired CORE site comparisons of both deposition velocities and dry deposition fluxes.

Goal: To provide detailed data on dry deposition at a limited number of regionally representative sites, and to test and improve methods used in routine measurement programs.

Chemical focus: Species for which more direct measurement methods are appropriate --- SO_2, O_3, NO_2, HNO_3, fine particles.

Siting: Regionally representative sites with uniform surface, and with existing research capabilities for application of different measurement methods.

2. Model Development

Several distinctly different levels of modeling activity can be identified for both the CORE program and the effort directed to develop dry deposition modules for regional models. Detailed sub-canopy models are presently in use to investigate the roles of dynamic processes in the deposition process, and to derive stand-level stomatal resistances from leaf distribution and solar radiation data. These detailed diagnostic models are used to generate a "big-leaf" model, in which the morphological and biological characteristics of the vegetative species representative of target areas are combined in a simple multiple-resistance code designed for routine application. (In practice, this big-leaf model forms the basis for the inferential method of deposition measurement, as described above. For dry deposition modules in regional models, the model is further simplified to a single surface resistance; in this case, the range of contributing surface processes is not always explicitly identified.

3. Process Studies

Micrometeorological field investigations are intended to identify the processes controlling deposition to natural surfaces, and to provide parameterizations of the relevant processes. The deposition velocity schemes used to infer dry deposition from routine observations of air chemistry and supporting meteorological and surface data and to

derive dry deposition in Eulerian dispersion models are constructed as a combination of these process specifications. Such micrometeorological studies have the unique benefit of examining the deposition phenomenon in a holistic manner; however, the number of chemical species that can be considered is very limited (O_3, SO_2, HNO_3, NO, NO_2, and some particulate species). Related field investigations are conducted at regular intervals at the CORE research sites, and at other locations also selected to provide the opportunity to address process-related questions (e.g., regarding the role of snow on a vegetated surface).

Chamber studies in field and laboratory environments are conducted as part of research programs primarily concerned with research on effects. However, the results of these experiments are critical to the formulation of deposition models. They can provide detailed data on important physiological factors which influence deposition processes on chemical species that cannot yet be studied using other techniques, and on a wider range of genotypes under controlled conditions. Moreover, careful manipulative studies can reveal the various roles of biotic and abiotic factors in governing deposition to plant canopies.

IV. CONTROLLED EXPERIMENTS AND ASSOCIATED MODELING

A. Introduction

Before proceeding with detailed examinations of different methods by which dry deposition can be measured in field situations, it is desirable to examine the factors that influence dry deposition in more detail. The background material given above summarizes the "state of the science" as seen by workshop participants. The following section addresses in more detail a number of factors that influence dry deposition. The context is that of modeling. In essence, dry deposition is the net result of many poorly-understood processes. This section deals with the most important of these processes, as reviewed by the working group on controlled experiments and associated modeling.

Attention was focused on the limitations and needs of dry deposition models. The group took the view that research should be directed not only to developing better methods to measure dry deposition rates, but also to understand the underlying physical, biological, and chemical processes governing atmosphere-surface exchange. This dual approach is necessary because measurements of dry deposition are inevitably restricted to a subset of situations, on the basis of which we must describe deposition regimes in other circumstances. While to some extent observations can be generalized empirically, the validity of such extrapolation is limited and ultimately suspect unless supported by theoretical understanding.

As a specific example, knowledge regarding trace gas deposition is presently limited to a small number of gases (mainly O_3, NO_x, HNO_3, and SO_2) for which some appropriate measurement techniques exist. For other gases (e.g., H_2O_2), suitable methods do not yet exist, and it is necessary to model dry deposition entirely by consideration of fundamental processes.

It should be emphasized that the process of dry deposition of gases is a subset of the process of air surface exchange of gases; i.e., exchange is a two-way process. The meeting restricted its concern to the deposition process in view of the fact that sources of atmospheric gases are the domain of other components of NAPAP.

There are three distinct levels of model applications -- (i) the estimation of dry deposition as a product of larger numerical models, (ii) the calculation of dry deposition from measured concentration information, and (iii) the site specific characterization of deposition in specific landscapes of ecological interest. In all three cases, adequate parameterization of the contributing processes is critical, requiring that the most important mechanisms be identified, and subsequently characterized in a manner that is compatible with the application.

Resistance models provide a convenient but limited framework for combining descriptions of the separate processes that contribute to the dry deposition phenomenon. The multiple-resistance approach is an extension of the vertical diffusion methods developed in meteorology (especially in agricultural meteorology); extension to situations of significant flux divergence, advection, or interceptive deposition presents conceptual difficulties and imposes errors that are presently difficult to quantify. This working group concentrated its attention resistance analog as guidance. It was accepted as an over-riding principle that basic research is necessary to reduce the great uncertainties arising in circumstances where turbulent diffusion is not the dominant aerodynamic mechanism of transfer between the atmosphere and the biosphere.

While atmospheric concentrations of pollutants are important parameters to characterize, these parameters are of limited value in efforts to understand (i) atmospheric processes governing sources and sinks of atmospheric chemical species and (ii) the contribution of dry deposition to the input of pollutants to terrestrial and aquatic ecosystems. It is imperative that the deposition velocity also be characterized in order to infer deposition rates given atmospheric concentrations. Unfortunately, the deposition velocity parameter, V_d, is not a constant but varies widely in both space and time, even for a single chemical species. The variability in V_d can be attributed to changing environmental conditions and biological features that govern the effectiveness of surfaces as sinks for gases and particles. The most important biological surface for deposition and the one most subject to change is the canopy composed of multiple layers of foliage.

For use in regional acid deposition modeling, more accurate dry deposition velocities are needed, for a range of surface types and conditions, for the following species:

SO_2 and O_3 (especially for dry surfaces)

NO and NO_2

Sub-micrometer particles (in at least 4 size ranges)

PAN, HCHO, and other organics (acids and peroxides) whose removal might proceed at intermediate rates.

There is no clear consensus regarding the magnitude of uncertainties associated with the deposition velocity parameterizations used in modern transport models. In some circumstances, large errors are conceivable. An attempt was made to quantify the uncertainties with the following results.

SO_2 and O_3: For some areas, computed dry deposition fluxes could be wrong by a factor of two or more, especially over non-simple surfaces (e.g., complex terrain, or a mosaic of surface and vegetative types). Considerable overestimation may occur (with current estimates) if surfaces become saturated with SO_2, e.g., during pollution episodes.

NO and NO_2: In some situations, deposition velocities could be wrong by as much as factor of three to five, for reasons similar to those given for SO_2 and O_3. Moreover, artifacts in the measurement of concentration may cause additional error in the measurement of NO_2 deposition.

Sub-micrometer Particles (deposition as a function of particle size): At present, there remains an order of magnitude discrepancy between field data obtained via some experimental techniques over some surfaces and the predictions of modeling studies (wind tunnel and theoretical), with the latter being supported by field experiments in other situations.

PAN and other organics: Few data are available; consequently, the reliability of current estimates is unknown.

B. Sources of Uncertainty

A number of areas were identified in which knowledge is not yet adequate to produce process parameterizations that are well accepted, for either long-range transport modeling or for assessment of dry deposition from measurements made at a target area. In each instance, recommendations concerning needs for immediate research attention were identified. More detailed descriptions of the relevant problems and of research proposed to help improve the present state of knowledge are given later.

- Atmospheric Transfer. Knowledge of the way in which terrain modifies aerodynamic resistance is greatly deficient.

- Scaling-up. In essence, field observations are relevant to an area of limited size near the point of observation. Often, as in the case of modeling or of studies of regional budgets, averages over much larger areas are required. Methods by which local measurements can be extended to provide larger-scale area averages have yet to be developed.

- Scaling-down. Field measurements made above a surface cannot yet be related with confidence to measurements of deposition to

individual surfaces which make up the canopy.

• Near-surface Chemistry. Measurements of dry deposition made above a surface (as by micrometeorological methods, for example) can be influenced by near-surface chemical reactions in some instances. The matter is likely to be of special importance in the case of nitrogen species, and possibly for gross particle exchange.

• Surface Wetness. There is strong evidence that condensation accelerates the deposition of sulfur dioxide, and limits that of ozone, much as expected on first principles. However, there is also evidence that surface wetness resulting from precipitation causes substantially different behavior. There is need both for sensors to detect when the surface is wet, and for improved methods to make use of the information.

• Saturation. A surface that is exposed to some particular pollutantfor an extended period may become saturated with respect to that pollutant and deposition velocities may become much lower than would otherwise be expected.

• Cloud-droplet Interception. This mechanism is acknowledged to be a major factor contributing to effects on alpine forest ecosystems. The processes by which cloud droplets are intercepted by a canopy are similar to those involved in the case of conventional dry deposition, and are of corresponding relevance here.

• Slow Deposition of Aerosols. The small deposition velocity of small particles is sometimes taken to be sufficient to relegate particles to a much lower level of importance than trace gases. In fact, the slower deposition of aerosols results in longer atmospheric residence times, and therefore raises such particles to a higher level of importance if the subject is long-range transport rather than more local effects.

• Biological Indicators. Vegetation under stress responds differently to external stimulae than if unstressed. Detection of a stressed situation is difficult. Recent work on biological indicators indicates some promise that stress might be detected through measurement of trace gases emitted when plants are in a stressed condition.

C. Atmospheric Transfer

Atmospheric transfer is traditionally characterized using a resistance analogy, in which exchange through the air is quantified using two coefficients -- R_a (aerodynamic resistance) and R_b (boundary or diffusion sublayer resistance). By analogy with water vapor transfer and by application of standard micrometeorological relations describing vertical turbulent transport, a logical theory is invoked to express R_a and R_b in terms of atmospheric quantities that can either be

measured in the field or predicted in numerical models. In practice, a third resistance component, R_c, is used to describe the efficiency of uptake by the canopy (or at the surface), once the depositing material comes in contact with receptors. For soluble trace gases, for example, R_c may be dominated by stomatal resistance.

The turbulent aerodynamic resistance R_a can be related to such factors as surface roughness, wind speed, and dynamic stability, using relations developed (and verified) in studies of the vertical exchange of heat, moisture, and momentum. The usual expression relates the resistance to the friction velocity (u_*), height (z), and stability (z/L; expressed as the ratio of the height z to the Obukhov length scale of near-surface turbulence L):

$$R_a = [1/(ku_*)].[\ln(z/z_o) - Y(z/L)] \qquad (1)$$

Here, k is the von Karman constant, and z_o is the surface roughness length associated with momentum transfer. The roughness length varies from surface to surface, but k is a characteristic of turbulent exchange in any situation (k = 0.4). The function Y(z/L) is derived empirically. In near-neutral stability, Y(z/L) = 0 and a resulting approximation to (1) is

$$R_a = U/u_*^2 \qquad (2)$$

where U is the wind speed at the height of interest.

The same micrometeorological experiments have led to a specification of the "quasi-laminar" boundary-layer resistance R_b that introduces the concept of a roughness length (z_{oc}) specific to the pollutant being considered. The expression for R_b is a reflection of the fact that the pollutant exchange characteristics of a surface differ from those associated with momentum exchange. A common form for R_b is then

$$R_b = [1/(ku_*)].[\ln(z_o/z_{oc})]. \qquad (3)$$

Wind tunnel measurements, laboratory studies, and a variety of theoretical arguments have been used to study the pollutant-specific features of exchange across the quasi-laminar sublayer. These investigations lead to an alternative (and frequently preferred) expression for R_b:

$$R_b = [A(Re_*)/(ku_*)].(Sc/Pr)^a \qquad (4)$$

where $A(Re_*)$ is a function of the surface roughness Reynolds number (Re_*), Sc is the Schmidt number, and Pr is the Prandtl number. The exponent a is variously assumed to be somewhere in the range 0.5 to 0.8, with most workers accepting a value of about 2/3.

A multitude of complicated intracanopy turbulence processes contribute to the coefficient R_b. Based upon measurements of standard meteorological variables over vegetated surfaces, it is usually assumed

that the coefficient A is a very slowly changing function of Re_*, with a value of about 2.0 for typical vegetated surfaces. The near-constancy of the coefficient A is thought to be due to slowing of the mean flow inside the canopy by the roughness elements. It should be noted that (4) is not appropriate for large particles, whose inertial impaction reduces R_b.

For homogeneous surfaces in flat terrain, the aerodynamic resistance R_a is quite well understood. However, specification of the deposition velocity of chemical contaminants and particulates to a canopy also requires accurate knowledge of R_b, which requires further study. To this end, wind tunnel studies and "controlled" or well characterized experiments in the environment should combine flow and air exchange definition within and above the canopy with chemistry and aerosol characterization. This is particularly necessary for deep canopies where canopy density and depth influence how long various elements within the canopy are exposed to gases and aerosols.

Where atmospheric resistance is limiting, i.e., where the canopy quickly and completely assimilates gases or aerosols delivered to it (e.g., HNO_3), the resistance involving transport within the canopy is of little consequence. Similarly, where the surface resistance is limiting, investigating R_b is not a high priority. However, many gases and certain size ranges of particles are intermediate in their interaction with the surface. The flow features transferring gases and aerosols between the canopy and the overlying atmosphere are important to define in these cases. For the special case of flow over and atmospheric transfer through a canopy for which the characteristics change abruptly, the evolving profiles which develop over and within the "second" canopy reflect the change in the resistance components R_a, R_b, and R_c. A study of these evolving profiles for quickly and slowly depositing contaminants as well as the changing wind profiles should permit evaluation of these resistance components as a function of the atmospheric transfer properties and surface characteristics defined as in the experiment.

There is need to consider both the uncertainty associated with the specification of the atmospheric resistances (R_a and R_b) and the uncertainty associated with the dry deposition flux that is computed using them. Large uncertainty in R_a (or R_b) does not necessarily

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Estimated average uncertainty in the derivation of R_a and R_b over one-hour and 100 m time and space scales.

	State-of-the-science Micrometeorology	Monitoring Observations	Grid Model Outputs
R_a	10%	20-40%	>40%
R_b	25%	50%	>50%

translate into great uncertainty in dry deposition, since the surface "canopy" resistance must also be taken into account; the nature of the surface is of importance. Here, the uncertainty will be evaluated in three ways: how well does this model represent the "true" value on a 100 m horizontal scale given inputs at several levels of complexity, corresponding to (1) state-of-the-science measurements of the fundamental micrometeorological properties, (2) routine on-site measurements of comparatively simple variables tailored to provide a good estimate of the atmospheric resistances, and (3) inputs derived as grid-scale averages from a mesoscale model.

There is a further uncertainty corresponding to the fact that existing knowledge of R_a and R_b is limited to relatively simple cases. In particular, the expressions given above for R_a apply only in so-called micrometeorologically acceptable situations of flat, uniform surfaces in stationary conditions. Complex terrain, surface complexity, and time variability all impose complications that are beyond the reach of existing understanding.

At this time, important contributions would result from increased research on the deposition of highly reactive gases and aerosols to wet surfaces (to provide information relating to R_a, potentially in situations more complicated than standard micrometeorological methods can address), and on the flux of sub-micrometer particles and high molecular weight gases (to help improve the formulation of R_b).

D. Scaling Up

Ultimately, the uncertainty of importance is the uncertainty in point estimates or patterns supplied to those who use the information directly in dose-response functions. Uncertainty estimates at the process, canopy, or microscale level that are not scaled up to correspond to the outputs necessary to assessment will be of limited utility to the policy makers, because of the corresponding uncertainty concerning overall cost-benefit analyses.

Dry deposition measurements are usually performed in areas of homogeneous land type, for which statistical properties of several surface and meteorological properties can be considered constant over relatively large areas. Effects associated with the transitional regime of deposition patterns due to abrupt changes in land type are carefully avoided in most field studies of dry deposition. Over large areas of the northeastern United States, land types are highly heterogeneous, and thus two problems can arise when extrapolating observed behavior to regional scales. Firstly, "edge effects" may introduce significant deviations, most likely enhancements, in dry deposition. Secondly, variability in land type will introduce significant chemical and meteorological variability over relatively small space scales. Thus, measurements or model predictions of dry deposition made over particular areas may not be representative of surrounding regions of different land types.

The uncertainties introduced by neglecting these heterogeneous effects when making regional scale or long term dry deposition

estimates are not known. Maximum errors in dry deposition estimates are expected when transport of pollutants to surfaces is determined by the turbulent transport in the lowest atmospheric layer. For regional models of acid deposition, these sub-grid variations in dry deposition are difficult to account for, although it is felt that these errors can be quantified through the use of higher resolution model, laboratory or wind tunnel studies, and possibly field studies of dry deposition into heterogeneous canopies. Data may already be available from aircraft observations of ozone flux over different land types to analyze these heterogeneous effects. Laboratory and theoretical modeling studies are relatively inexpensive, and can be expected to yield useful insights into these phenomena. Field studies, in addition to being expensive, would not be expected to yield results which are generally applicable over large areas.

E. Scaling Down

The issue of scaling down focuses on several process levels subsequent to turbulent transfer to the canopy and includes the physical, chemical, and biological (e.g., leaf surface properties) factors governing the deposition and fate of trace gases. The rationale for this effort is based on the tenet that canopy surface properties limit dry deposition of many airborne chemical species to forest and crop canopies. In scaling down from above the canopy, three coupled areas are identified:

1) deposition processes at the stand level,

2) deposition processes at the whole-leaf level, and

3) linkage between deposition at the whole-leaf level and plant physiology.

The greatest sources of uncertainty underlying the issue of dry deposition to vegetation canopies are twofold and will require simultaneous effort in order to resolve the major contributions. The first concerns the factors (biotic and abiotic) governing the deposition of gases to individual leaves; this will help resolve the temporal and spatial variation that governs the deposition processes. The second area is the linkage between deposition and plant response at the physiological level; this will establish a formal mode of communicating deposition rates to the physiological and ecological community. The magnitude of uncertainty in each area is highly dependent on the chemical species, with considerable data available for some compounds (e.g., O_3, SO_2, NO_2) but essentially no data for the majority (e.g., NO, H_2O_2). For most compounds, we can assign an uncertainty of two orders of magnitude to deposition rates to individual leaves. The uncertainty in linking the processes of deposition to physiological response cannot be quantified at this time.

The major concerns of areas of uncertainty are outlined for each area beginning with the canopy/stand level and proceeding to the linkage between deposition and plant response.

1. Deposition Processes at the Stand Level

In general, modeled and measured SO_2 fluxes agree well above forest and agricultural canopies (r^2 = 0.4 to 0.6, using half-hour averaged data). This includes both the "big leaf" and more detailed canopy models (resistance and higher-order closure). Due to geophysical limitations, agreement between half-hour modeled and measured fluxes cannot be expected to be better than about ±30%. The turbulent transport phenomenon is statistical in nature, and hence the agreement between predictions and observations should improve as the averaging time increases. If flux comparisons are based on weekly periods, for example, the accuracy would be considerably better (possibly nearing 10%). The main uncertainty lies in characterizing the surface (leaves or soil) sink/source strength which usually involves estimates of stomatal resistance, soil resistance, and cuticular resistance. Although the cuticular and stomatal resistance terms vary substantially as a function of the environment (e.g., surface wetness), species characteristics, and temporal features (e.g., diurnal, seasonal), our knowledge of how these factors interact is fragmentary.

Focusing more attention on better characterizing the leaf surface and soil resistance terms is a viable research goal. Effects of surface wetness, pollutant concentrations (chemical stress), water stress, time of year, and mesophyll resistance on the overall surface resistance term need to be addressed. Continuous evaluations of canopy (or big leaf) models for various types of canopies and surfaces need to be carried out using direct measurements of chemical fluxes. Also, the possibility for models to deal with bi-directional fluxes of chemical pollutants (such as NO_2) should be considered. Measurements separating the total chemical deposition into leaf surface and internal fractions and the fraction absorbed by soil need to be conducted, since model results indicate that the soil fraction can be as large as 25% of the total landscape flux for reactive trace gases.

2. Deposition Processes at the Whole-Leaf Level

Because the leaf offers a variety of physical sites for deposition (e.g., leaf surface vs leaf interior, mesophyll cell vs guard cell) and each site is chemically different, deposition rates are likely to vary substantially as a function of the chemical properties of the trace gas and their foliar sites of deposition. While substantial bodies of data exist on a few of the more common gases (e.g., O_3, SO_2, NO_2), data do not exist for the remainder with respect to the range of deposition rates to foliar surfaces. Rates are likely to vary by several orders of magnitude as a function of solubility in water, chemical reactivity in solution, and reactivity with lipid/cuticular surfaces.

While the deposition process at the whole canopy level can provide estimates of a chemical's deposition to foliar surfaces, it cannot routinely discriminate deposition to the leaf surface versus the leaf interior. The site of deposition, particularly the component of flux through the stomate, is particularly important to the physiological community because sites of toxicity are in the photosynthetically active cells of the leaf interior.

Each gas exhibits a range of deposition rates that vary spatially (e.g., different landscapes, vertical position in canopy) and temporally (e.g., diurnally, seasonally) over many orders of magnitude. The variation is not due to (or indicative of) residual error, but rather a consequence of the interplay of biotic and abiotic factors. The degree to which these factors, individually and in combination, affect deposition is fragmentary. The specific sources of variation requiring research are: (1) climate (e.g., temperature, vapor pressure deficit, light), (2) atmosphere (e.g., trace gas concentration, trace gas co-occurrences), (3) soil (e.g.., soil moisture, nutrient status), and (4) biology (leaf surface morphology, phenology, growth form, water potential, etc.).

The resolution of how each of these sources affects deposition rates to foliar surfaces must be integrated via modeling efforts that relate the influence of each physical, chemical, and biological factor to functional processes operating on the leaf surface or leaf interior. This includes parameterizing cuticular resistance, stomatal resistance, mesophyll/residual resistance, and chemical potential gradients in the gas and liquid phase. This modeling (e.g., resistance analogy) must be integrated subsequently with the whole canopy/stand level modeling effort.

3. Linkage of Deposition to Plant Physiological Processes

The accurate analysis of deposition at the whole leaf level including an estimate of the distribution of deposition sites on the leaf surface and leaf interior will help resolve the effectiveness of vegetation canopy in removing trace gases from the atmosphere. However, considerable uncertainty exists in relating this deposition to the physiological status of the plant.

The specific areas of uncertainty are (1) chemical dynamics of deposition in the gas and liquid phase (e.g., pool sizes, scavenging of gases in gas and liquid phase, enzymatic reactions and sequestering/detoxification), (2) physical/morphological fate of deposition, (3) physiological sites of initial metabolic dysfunction/mechanism(s) of action, and (4) interactive effects with other factors affecting physiology.

The types of controlled experiments to address these areas of uncertainty are trace gas-specific. In terms of deposition to foliar surfaces, methodologies exist for both laboratory and field efforts and in the latter include both enclosures (chambers) and open vegetation canopies. The types of systems for controlled laboratory studies include whole-plant deposition chambers, individual leaf cuvettes, split-leaf cuvettes, and radiochemicals. Many of these can be made portable for field application in forest or crop canopies. The linkage of deposition to measuring the physiological status of the plant, particularly for gas-exchange properties (e.g., carbon dioxide assimilation, transpiration) is routine. The uniqueness and challenge lies in developing systems for accurately characterizing trace gas deposition. The application of radiochemicals and stable isotopes to field efforts warrants consideration.

F. Near-Surface Air Chemistry

Flux measurements assume that the observed temporal or spatial changes in concentrations are primarily indicative of the surface flux itself. If there are changes in concentration due to chemical reactions, then this assumption will be flawed. Therefore, if the chemical lifetime of the species of interest is on the order of the time scale of the period it takes to make the flux measurement, then the chemical loss or gain rate must be accounted for in order to obtain accurate fluxes. Otherwise, the potential uncertainties could be as large as 50 to 100%.

For those species that represent high-priority needs for deposition fluxes, three have chemical lifetimes that are short enough that losses must be accounted for in the flux measurements.

1) Nitric oxide (NO). There is a rapid (of the order of seconds) loss of nitric oxide by reaction with ozone,

$$NO + O_3 \rightarrow NO_2 + O \qquad (5)$$

The rate constant is well known; even its temperature dependence has been determined.

2) Nitrogen dioxide (NO_2). Nitrogen dioxide is photodissociated by sunlight with a lifetime of the order of minutes:

$$NO_2 + h\nu \rightarrow NO + O, \qquad (6)$$

The photolysis rate has been studied both theoretically and experimentally and is well known.

3) Ozone (O_3). Ozone is lost by chemical reaction with a variety of other atmospheric species [e.g., Eq. (5) above], but at rates that require the reactant concentrations to be substantial before the chemical lifetime approaches the size of the measurement period. An example of such species whose concentrations could possibly be sufficiently large to pose an interference is the naturally emitted volatile organic compounds, e.g., isoprene and terpenes, which may be abundant within forest canopies.

Prospects for improvement appear good, and immediate scientific attention to the problem is likely to be profitable. The effects have been studied and formulated. Future field experiments of the atmospheric fluxes of the relevant chemical species should take into account the relevant chemical processes (as outlined above) in the data reduction operation. The chemical terms will generally require supporting measurements, e.g., $h\nu$ and T for NO and organics for O_3. Frequently, the supporting measurements would be made for other reasons. Hence, the accounting for chemical losses often may not be a large additional expense.

G. Surface Wetness

Surfaces can be wetted by dew, rain or deposited cloud water. Deposition rates of gases and particles to wet surfaces may differ from those to dry because: liquid films replace surface sinks such as cuticle or stomatal pores; liquid films may dissolve surface contamination, or exchange ions with leaf interiors, thus altering the sink strength for gaseous pollutants; on wet surfaces, interactions between deposited pollutants (e.g., H_2O_2 and SO_2) may alter the sink strength; wet surfaces absorb the momentum from large particles which may otherwise "bounceoff" when impacting in strong winds.

Because they are usually in equilibrium with concurrent gaseous pollutants, cloud water and rain are, when present on surfaces, unlikely to represent strong sinks. However when rain or cloud deposition ceases, altered gas concentrations in air (e.g., H_2O_2) may be transferred to surfaces and allow rapid deposition of SO_2. At the same time, chemical exchange within leaves may buffer leaf liquid films to allow them to be strong sinks. Concentrations of dissolved ions in cloud water are typically greater than in precipitation giving rise to a higher damage potential.

In contrast, dew is not initially in equilibrium with atmospheric gases, and so enhanced deposition rates of gases are likely both during dewfall and after dewfall ceases (when buffering mechanisms the same as for rain and cloud water apply).

A major uncertainty is the present poor knowledge of the duration and spatial distribution of wetness. Duration depends on the interception capacity of foliage and micrometeorology (evaporation). Spatial distribution varies with plant species and with the type of wetness (dew providing a more uniform cover than precipitation).

The uncertainty introduced in deposition estimates by uncertainty in surface wetness may be very large for individual events (perhaps an order of magnitude). For longer-term deposition, surface wetness introduces the largest uncertainties when present at times of large deposition rates (e.g., during day, after rain). Deposition rates are often limited by atmospheric transfer when there is dew, and so uncertainty during these periods may not be strongly reflected in long term deposition, so the overall uncertainty may be about 50%.

Considerable improvement in the state of knowledge would result from the development of wetness sensors simulating various foliage types (wetness sensors should be able to differentiate between cloud, precipitation, and dew events and should record the period of wetness following cloud and precipitation exposure. Controlled experiments in chambers could quantify effects of foliar wetness on deposition rates of particles and gases singly and in mixtures (for example SO_2 in the presence and absence of H_2O_2). Existing canopy models of wetness duration could be used to improve estimates of deposition.

H. Cloud Droplet Deposition

Instrumentation exists to measure the concentration and size distribution of cloud droplets. From such measurements the liquid water content of clouds can be calculated and compared with independent measurements of cloud liquid water content. Uncertainty for liquid water content, measured directly, is about 25% under excellent experimental conditions. Uncertainties for cloud droplet size distribution measurements and subsequent conversion to liquid water content are somewhat larger but certainly better than 50%.

Cloud droplet interception onto well defined surfaces such as cylinders and spheres is well known and controlled by the Langmuir stopping distance. The main controlling parameter for cloud interception is the relative velocity between cloud droplet and inceptor surface, i.e. the wind flow on a micrometeorological scale. While it is possible to model this process quite accurately, a major "unknown" in the environment results from the unknown flow of air around irregular shaped foliage. Deposition of cloud water to the top of a uniform canopy can be estimated from current knowledge of micrometeorology, probably with an uncertainty factor of two to four. Additional uncertainties introduced by complex topography and complex canopy structures (dominant trees, etc.) increase the uncertainty in estimating deposition to most field sites to a factor of about 10. Improvements would arise from studies of air flow in relation to canopy structure, and from experiments to investigate the efficiency of isolated trees and forest edges in capturing cloud water.

I. Particle Deposition

Although most discussion concerning effects of pollutant deposition emphasizes the roles of trace gases (especially SO_2, O_3, NO_x, and HNO_3), the importance of particles cannot be overlooked. It is known, for example, that super-micrometer aerosol particles can deliver a substantial fraction of the nutrients (especially NO_3^-, NH_4^+, $PO_4^=$, K^+, Ca^{++}, and $SO_4^=$) for forest and aquatic ecosystems. Furthermore, deposition of some sub-micrometer trace elements (especially heavy metals such as Pb and Cd) can be toxic to such ecosystems.

Direct impaction of polluted (e.g., acidic) cloud droplets on forests, especially on trees at forest edges, may contribute substantially to tree damage.

Some materials (e.g., marble) may be damaged by the deposition of particles that catalyze the oxidation of SO_2, subsequently leading to pitting of the material at the site of the catalytic particle.

Finally, from the view of long-range transport modeling and associated predictions of the consequences of pollution controls, there is great need to determine the dry deposition of sub-micrometer particles, as functions of particle size and surface characteristics.

The importance of the last application listed above, for modeling, seems to need additional explanation. It appears possible that the deposition of sub-micrometer particles may be of special importance in the context of long-range transport modeling because the deposition is relatively slow. Corresponding to a deposition velocity range from 0.5 to 0.05 cm/s, time scales of atmospheric residence (over which long-range transport can continue) range from about 1 to 10 days, and distance scales are from about 250 to 2500 km. Hence, one of the important features of the long-range acidic deposition problem is the slow dry deposition of, e.g., sub-micrometer sulfate particles and their availability for deposition in precipitation far downwind.

Currently, there remain substantial uncertainties about particle dry-deposition. Some of the major uncertainties are described below.

1. Sub-micrometer Particles

From wind-tunnel, theoretical, and some field studies, a general picture of the dry deposition velocity as a function of particle size and surface characteristics has evolved. The results show a broad minimum in the deposition velocity, down to values near 0.01 cm/s, for particles of size near 0.1 μm. For smaller particles, the dry deposition velocity increases with increasing Brownian diffusivity; for larger particles, interception, inertial impaction and gravitational settling increase the deposition velocity (although a secondary minimum can occur for particles of size near 5 μm, caused by particle bounce-off). For the minimum near 0.1 μm, the remaining contribution to collection is from interception, although particle growth by water-vapor condensation and diffusion- and electro-phoresis can contribute to particle deposition for some situations. In contrast to this picture, some field data using eddy-correlation techniques show no significant minimum in the deposition velocity for sub-micrometer particles: these studies yield considerably larger deposition velocities. The cause(s) of this discrepancy need to be identified and the uncertainty removed.

2. Super-micrometer Particles

Three of the major uncertainties about the dry deposition of super-micrometer particles deal with sampling, particle bounce-off, and summing over many collectors. (1) Progress is currently being made in the sampling of super-micrometer particles at ground sites; more progress is needed before reliable, isokinetic samples of super-micrometer particles can be obtained by aircraft; such samples are highly desirable because ground-level samples of super-micrometer particles are strongly affected by local sources. (2) Quantitative descriptions of particle bounce-off, as a function of surface type and conditions, are not yet available. (3) The problem of summing the deposition of super-micrometer particles, or testing available models of this summing, for the deposition to an entire tree or a forest edge or an entire forest, requires additional field studies.

From the list of current uncertainties, a number of near-term studies can be identified. All of these studies should include a substantial commitment to

theoretical and numerical modeling. The list of studies follows; it should be possible to complete all studies listed within the time available to NAPAP.

- Field studies should be conducted of the deposition of cloud droplets to vegetated surfaces. Especially productive studies would involve the collection of supercooled cloud droplets at high-altitude locations.

- Classical wind tunnel studies of particle deposition to ideal non-ideal) surfaces should be conducted to extend knowledge to a wide variety of substrates, with different texture, orientation, and composition. Special attention should be directed to the matter of particle bounce-off.

- Field studies of the advective (interceptive) deposition of sub-micrometer aerosol particles at the edges of forest stands should be initiated. Studies could make use of tracer releases (of "tagged" particles of well-controlled size), of in-canopy gradient measurements (both horizontal and vertical), and of intensive studies of the deposition to elements of the canopy (e.g. using electron micrography).

- Large-scale studies of the deposition of natural aerosol trace opportunity" such as sea-salt aerosol should also be considered.

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V. SURFACE ANALYSIS METHODS

A. Introduction

Environmental surfaces, although difficult to simulate either mathematically or physically, naturally integrate the net effects of dry deposition of various atmospheric constituents. Surface analysis methods can be used to quantify the amount of deposited material residing on such surfaces. From knowledge of the area of the surface in question and the duration of the period during which dry deposition occurred, the net dry deposition rate to the surface being analyzed can be computed.

The objectives of the working group on surface analysis methods were as follows:

- To critique various surface analysis approaches for their capabilities in routine and research modes; and determine their limitations, addressable chemical species, accuracy, and the time until useful results can be expected.

- To recommend a research program for NAPAP to address needs in dry deposition measurements, and an extension of this program beyond NAPAP in the general area of atmosphere/canopy exchange processes.

- To outline key experiments which should be performed prior to or concurrent with the planning of any large scale application of these dry deposition methods.

Conclusions drawn by the Working Group are summarized at the end of this section, where a table is given concerning the applicability of existing surface-analysis techniques for measuring dry deposition and the potential for rapid development of new methods of measurement.

B. Foliar Extraction

This method measures material deposited on live plant surfaces by using selective extraction procedures to separate this material from internal plant pools. Net changes in the surface area concentration of these constituents during dry conditions of known duration are used to calculate dry deposition to foliage exposed under field conditions. The method has been demonstrated for deciduous foliage, pine needles, agricultural crops, and whole tree seedlings.

1. Applicability

Space scale -- Individual leaves (cm^2) to groups of leaves (m^2); can be scaled to individual plant canopies with further research (see below).

Time scale -- Tens to hundreds of hours.

Chemical Species -- The method has been demonstrated for particle-associated $SO_4^=$, NO_3^-, major cations, and some trace metals. The extraction of deposited SO_2 and HNO_3 has been suggested in some studies.

2. Strengths and Weaknesses

Foliar extraction involves direct analysis of actual plant surfaces exposed under field conditions and is particularly useful for studies of dry deposition distribution within canopies. The extraction procedures have been successfully demonstrated to selectively remove surface deposits from conifer and hardwood foliage both intact and removed from the plant, from crop foliage, and from tree seedlings

exposed in wind tunnels. The method can provide useful data for studies of the extrapolation from point measurements and of in-canopy modeling.

Spatial and temporal variability in the field can be assessed using foliar extraction methods can be tested for recovery by dosing leaves with known amounts of "deposited" constituents, and the analytical results can be checked by charge balance and conductivity calculations.

The method requires access to leaves distributed throughout the canopy (easy for crops and seedlings, but requiring towers for forests). The sampling requirements can be labor intensive for large-scale studies, requiring the handling and analysis of large numbers of leaves. The behavior of deposited vapors and gases is uncertain, with conflicting data in the literature on the extractability of SO_2. To assess the effects of dry deposition alone, field measurements must be made in the absence of rain, fog, or dew drip.

3. Availability and Key Experiments

Data on particle dry deposition to plant surfaces and canopies can be available in the period of two to three years. The extraction efficiency for deposited vapors should be determined using isotopes under controlled conditions in laboratory and field chambers. The primary factors controlling extraction rates under different conditions, including the influence of plant nutrition status and time of year, are not well understood. The extraction methods need to be developed or tested for a wider range of plant surfaces (species).

C. Throughfall and Stemflow

The net flux of a substance in throughfall plus stemflow (TF + SF) beneath a canopy may be separable statistically into components representing dry deposition and canopy exchange. A regression analysis approach has been tested and found to give reasonable results for a deciduous forest canopy in the eastern United States. In this approach the net TF + SF for individual storm events was regressed against the precipitation volume and the length of the antecedent period (dry period prior to storm event), and the regression coefficient for the antecedent period term was used as a measure of the dry deposition flux rate.

Uncertainty of the estimate can be determined from the standard error of the regression coefficient. Note that if it can be shown that the canopy exchange component of net TF + SF is negligible (see Key Experiments below), then the TF + SF determination becomes the estimate of the dry deposition flux. This technique is applicable anywhere single-event samples of TF + SF can be collected. Analytical uncertainties are expected to be minimal and can be checked by charge balance of the solutions that are chemically analyzed. Potential biases in the technique should be ascertained experimentally, as discussed below.

1. Applicability

Space scale -- The smallest applicable space scale is that of an individual tree canopy, and the maximum scale is limited only by the logistical consideration of servicing a large throughfall network. The size of a typical forest research plot (hundreds of square meters) is probably a good practical scale.

Time scale -- The technique averages dry deposition rates over a period long enough to provide sufficient single event samples to perform the regressions. For most areas of the eastern United States, the shortest averaging period is probably on the order of two months, and the longest reasonable period is on the order of several years. In cases where it is demonstrated that foliar leaching is negligible, net TF + SF is a direct estimator of the dry deposition during the dry period prior to each event. In this case, the averaging period is on the order of several days.

Chemical Species -- K^+, Ca^{++}, Mg^+, Na^+, Cl^-, Total S (= SO_2 + $SO_4^=$; depending on the outcome of exploratory studies presently being conducted); perhaps NO_3^-, and H^+ in some cases.

2. Strengths and Weaknesses

The measurements that are required are inexpensive and not technically demanding, yet naturally integrate deposition to whole canopies over periods of a season or longer. In concept, the method is widely applicable, not being limited to specific areas of uniform terrain and homogeneous canopies. One set of TF + SF collections can be used to provide dry deposition estimates for many different ions. The measurements may also be useful for effects research. The technique can be simplified considerably if the mobility of internal foliage ions can be proved to be minimal. Recent studies of internal $SO_4^=$ behavior in trees using S-35 tracer indicate that only a few percent of the $SO_4^=$ flux beneath some hardwoods originates from internal S pools. In this situation, net throughfall flux is a direct measure of dry deposition wash-off.

Throughfall and stemflow measurements "see" only material removable by rain. Dry deposits which are irreversibly absorbed by the canopy, or deposited to areas of the canopy not washed by rainfall, are not measured. Sulfur dioxide, NO_2, and HNO_3 vapor are of particular concern regarding foliar absorption. Evidence available so far (based on exposure of foliage to sulfur dioxide carrying S-35 tracer) indicates that SO_2 deposited to the leaf cuticle can be removed by rinsing with water, and is hence available for removal and measurement in throughfall studies. On the other hand, SO_2 entering leaf tissue through stomata is not as available for extraction by rinsing the surface and hence is not measured completely in throughfall experiments. Thus, by careful selection of field exposure conditions, it may be possible to use the throughfall method to quantify primarily

particle $SO_4^=$ dry deposition or particle plus vapor forms of dry deposited sulfur oxides. In either case, the method measures the critical fraction of deposited SO_x that is not metabolized in the canopy, but that which reaches the ground as potentially acidifying $SO_4^=$.

Throughfall methods may not work for ions that are strongly absorbed by the canopy (e.g., H^+, NH_4, Pb^{++}, and some other trace metals). Possible complications exist from the exudation of internal foliar material during dry periods, from surface residue left over from previous rain events, and from slow washoff of dry-deposited materials. The influences of these factors are unknown but are not expected to be significant.

The assumptions that the canopy exchange component of net TF + SF is correlated with precipitation volume and that the dry deposition component is correlated with antecedent period have not been tested under controlled conditions. Because numerous (typically twenty) events are needed before a correlation analysis can be performed, a lag period exists between the start of the study and the estimation of dry deposition.

3. Relevance to Modeling and Effects Research

Throughfall techniques are especially relevant for effects research because they integrate over time and space scales appropriate for potential effects of atmospheric deposition. The ability to assess studies of dry deposition of basic cations is very useful for studies of soil and watershed acidification. The method may be useful for model verification to the extent that total S deposition (SO_2 + $SO_4^=$) can be used as a criterion.

4. Availability and Key Experiments

The technique has not been thoroughly evaluated. In particular, it has only been tested at one site in North America. Expanding the technique to more sites immediately may provide useful information, but investment of about two years' research into the experiments suggested below is advisable.

This method should be tested in more forest types, on more chemical species, and with better spatial replication of samplers than has been attempted to date. Some currently existing data may be applicable to this testing. The method can probably be improved by substituting dose (pollutant concentration x time) for antecedent period (time only) in the regression analysis. This would require air quality data at the site of the measurements of TF + SF. Other critical experiments are as follow.

- Foliar leaching should be investigated, especially its correlation with precipitation amount. A tree's sapstream could be tagged with a radioactively labeled ion and measurements made of the quantity of that ion found in TF + SF in a number of real or artificial precipitation events. Alternatively, plants could be grown in an environment free of dry deposition, such as an open-top chamber, and amounts of ions in leachate would be determined after artificial rain events of different volumes.

- The efficiency of removing dry deposits by washing should be studied, possibly using plants which have been experimentally exposed to different pollutant doses (varying both concentration and time of exposure) in an open-top chamber.

- The feasibility of extending throughfall techniques to studying the dry deposition of sulfur dioxide should be explored. In particular, the ability to remove deposited SO_2 by rinsing with water (as in the case of throughfall studies) should be studied; the binding of stomatally-transferred SO_2 in internal leaf tissue should be investigated.

- Different methods of assessing spatial variability of TF + SF should be tested to improve the ability to capture the variability in dry deposition while excluding noise generated by other canopy processes.

- Regression methods should be tested on forests of the same species in similar dry-deposition environments but on sites of different soil fertility to determine if variations in internal cycling of nutrients affect the estimates of dry deposition.

D. Cloud Droplet Collection

Relevant techniques were discussed only briefly at the workshop because cloud water was not explicitly considered. However, cloud water deposition is very important at high elevation sites and is not collected efficiently by standard wet deposition samplers, therefore, alternative methods are needed. Although micrometeorological techniques have sometimes been used to measure cloud-water deposition, (see discussion under part III.H), most areas of importance in the Eastern United States are sufficiently mountainous to make micrometeorological methods very difficult to apply. Measurement of throughfall and steamflow (TF + SF) during cloud events provides an inexpensive estimate of the deposition of water, which can then be multiplied by pollutant concentrations in cloud water collected above the canopy to yield a deposition rate for the pollutants. Deposition of TF + SF underestimates cloud water deposition by 10 to 20% because of evaporation in the canopy, but this bias can be corrected by estimating evaporation rates using meteorological data.

1. Applicability

Space scale -- Individual tree to forest stand

Time scale -- Event (hours to days)

Chemical species -- Any that occur in cloud water

2. Strengths and Weaknesses

This technique is applicable in mountainous terrain and patchy vegetation, is inexpensive and is not especially technically demanding. It gives a direct estimate of cloud water deposition.

Adequate sampling is necessary to account for spatial variability of TF + SF. The technique is not applicable in sub-freezing conditions, and it requires simultaneous measurement of cloud water pollutant concentrations, which can be difficult, especially in mixed rain/cloud events. The correction for bias due to evaporation requires collection of meteorological data under severe conditions.

3. Relevance to Modeling and Effects Research

Measurements of chemical deposition by cloud droplet impaction are necessary for effects studies at high elevation sites and are required to verify the deposition predictions of cloud water deposition models.

4. Availability and Key Experiments

The methods are immediately applicable; no outstanding problems remain to be addressed experimentally, although some of the reservations mentioned in the context of throughfall and stemflow are also applicable here (see Section 3.4.4).

E. Watershed Mass Balance

The watershed mass balance approach for calculating dry deposition entails the determination of the net mass flux of constituents by subtracting the wet precipitation flux from the basin export in streams and groundwater. The method is dependent on the identification and quantification of sources and sinks of the deposited constituents within the watershed and has been used to estimate sulfur and chloride dry deposition at a site in the northeastern United States.

1. Applicability

Space scale -- The gauged area should be 5-10 ha or larger to eliminate edge effects. It has been suggested that the mass balance approach could be used on a smaller scale (say 10 m^2) by using large lysimeters containing soil and plants and sealed at the edges to prevent horizontal transport.

Time scale -- The appropriate time scale is associated with the spatial scale, as smaller drainage areas generally have shorter water residence times. The method will not provide information on periods shorter than wet events (at best), with the most probable minimum time frame on the order of months. In practice, estimates of dry deposition are possible on a seasonal to annual scale.

Chemical Species -- The method can be used with conservative particle constituents (Cl^-, Br^-, and perhaps $SO_4^=$ in some instances) In the case of sulfur, it is possible to measure only the sulfate flux from the watershed. Relating this to inputs by both wet and dry deposition (of gases and particles) has not yet been demonstrated.

2. Strengths and Weaknesses

Watershed mass balances provide a large scale, integrated measure of deposition to multiple surfaces within a landscape. After initial calibration, the method can provide a long-term measure of dry deposition for trend testing.

Site selection criteria are demanding. The watershed must be a hydrologically tight system with quantifiable internal sources or sinks for the chemical species of interest. The initial characterization and instrumentation are expensive and time consuming. Advantageous characteristics not always apparent prior to instrumentation and calibration.

Detailed chemical speciation of deposited material cannot be determined.

3. Relevance to Modeling and Effects Research

Results obtained using this method can be used to test the validity of model predictions over distance scales up to tens of kilometers. The results can also be used for long-term trends analysis, and to establish boundary conditions for effects studies.

4. Availability and Key Experiments

The Leading Ridge experimental watershed in Pennsylvania is ready now. Other similar calibrated watersheds in the northeastern United States could also provide immediate data.

The Panola Mountain research site in Georgia can provide short-term fluxes from bare rock areas by the end of 1986, and longer-term average values by the end of 1987.

To select instrumentation and calibrate a new watershed would take 18 months, although data collection could commence immediately after site selection and instrumentation.

An experimental program is needed to determine the rate at which sulfur is cycled through the system, perhaps by using a combination of radioactive and stable isotopes, and with a focus on the chemical changes occurring through the watershed system.

F. Isotopic Tracers

Isotopic approaches can provide a clear distinction between material deposited from the atmosphere and surface materials derived

from other sources. The rate of accumulation of atmospherically-derived material may, therefore, be measured in a system in which surrogate or manufactured collectors cannot be used. A variety of processes operating over a range of time scales may be addressed.

1. Long-Lived and Stable Tracers

Direct measures of total wet plus dry deposition rates of sub-micrometer aerosols to natural surfaces may be obtained by measuring the inventories in soils of natural or fallout-derived immobile nuclides such as Pb-210 and Cs-137. A precision of 10% in total deposition rate is readily obtained, so that these nuclides can be used to verify the prediction of transport and wet plus dry deposition models.

For example, the ratio of Cs-137/Pb-210 is a factor of 2.2 greater in precipitation to the eastern United States than it is in surface air, due to a 10-fold increase in the Cs-137/Pb-210 ratio between the surface and the tropopause. Hence, the Cs-137/Pb-210 ratio in a soil is a function of the fraction of the aerosol deposition derived from surface air by dry deposition and cloud water impaction. This isotope ratio appears to be a fast and inexpensive method for determining the amount of "dry" aerosol scavenging from surface air at mountain sites. The Cs-137/Pb-210 ratio also allows testing of model prediction of enhanced dry deposition of sub-μm aerosols at the edges of forest stands in lowlands. Soil inventories of Cs-137 and Pb-210 accumulate over decades; the results based on their ratios, therefore, reflect long-term means, assuming some stability in local vegetation patterns, and assuming no edge effect on wet deposition.

Another potentially useful tracer pair is Sr-87 and Sr-86. The ratio of these two stable isotopes of strontium varies with bedrock lithology as a function of composition and age. At some sites, the Sr-87/Sr-86 of aerosols differs from that of the bedrock and vegetation. Sr is an analog of Ca and is typically carried by the coarse aerosol. When such a difference exists, the fraction of Sr in throughfall originating beyond the ecosystem and delivered to the canopy by dry deposition, may be accurately measured. This isotopic tracer can provide a sensitive, independent test of estimates of dry deposition provided by throughfall analysis techniques and has the added advantage of separating transported Sr from that originating by resuspension from within the ecosystem.

(a) Applicability

Space scale -- In general, the sampling scale is determined by the dimensions of the soil core that is used. Large area surveys are possible, and are relatively inexpensive.

Time scale -- Pb-210, Cs-137 - The technique integrates total (wet plus dry) deposition over decades.

-- Sr-87/Sr-86 - Variable from event for throughfall to

decades for entire watershed, depending upon site and sampling.

Chemical Species -- The methods are keyed to specific radioisotopes; chemical speciation of the particles involved in their dry deposition is not possible.

(b) Strengths and Weaknesses

These isotopes provide a unique identification of atmospherically derived material - there is no non-atmospheric source that could confuse the interpretation of the results.

The method provide fluxes for classes of material (i.e., fine particle, coarse particle) rather than for individual airborne species. For some isotopes, only total deposition can be measured.

(c) Availability and Key Experiments

Methods using isotopic tracers rely on previously developed techniques and may be used immediately.

2. Short-Lived Natural Tracers

Direct measures of dry deposition rates may be obtained by using natural radioisotopes whose half-lives are shorter or of the same order of dry periods. Such isotopes include Pb-214, Pb-212, and possibly S-35 and Be-7, all of which reside on predominantly sub-micrometer aerosols. Use of these nuclides involves sampling and measurement of individual surface components (leaves, etc.). The natural flux of S-35 from the atmosphere may be a particularly useful tool in depositio studies. This natural $SO_4^=$ tracer offers great potential in conjunction with studies of watershed mass balances, but the necessary methods are still under development.

(a) Applicability

Space scale -- The appropriate spatial scale is vegetation-surface specific (i.e, on the order of cm^2). Replicated sampling permits extrapolation to canopy scales.

Time scale -- These isotopes are appropriate for processes occurring over time scales from days (Pb-212) to months (Be-7).

Chemical Species -- The methods are applicable to sub-micrometer particles in general.

(b) Strengths and Weaknesses

This method provides a direct measure of dry deposition rates to foliage in the field. It has been used to evaluate within-canopy variation of air-surface transfer of sub-micrometer aerosols. Hence,

it can be used as a tool for testing model (parameter) requirements.

The method provides information only on generic classes of airborne material; it is not particle-size specific. It does not directly measure dry $SO_4^=$ flux. It can be highly climate dependent (e.g., in the case of Be-7, it can be applied only in arid climates). There is a limited time during which the analytical measurements must be made (e.g., Pb-212 has a 10 hr half life). Scaling up to whole canopies and beyond requires extensive measurements of both tracer concentrations and foliar biomass.

(c) Availability and Key Experiments

The isotope sampling and analysis techniques are readily available. However, one to two years of further testing are required to permit large-scale fluxes to be addressed. Capabilities to address leaf-scale deposition velocities are being developed now.

G. Snow Sampling

Snow sampling can be used to assess wet deposition, dry deposition, or total deposition, depending on the field procedures used. Measurement of the concentrations of contaminants in fresh snow can be used to determine wet deposition rates, while sampling these concentrations in surface snow as the snow ages will provide a measure of dry deposition. Sampling older snow, or sampling entire snowpacks and snowpack meltwater, yields total deposition.

1. Applicability

Space scale -- Snow sampling is point measurement; however, it is reasonably inexpensive to replicate a large number of points.

Time scale -- At least 1 to 2 days of dry flux are needed so that material accumulating on the surface from dry deposition is distinguishable from concentrations in the fresh snow. Analysis of snowpacks may provide total deposition integrated over a season.

Chemical Species -- The method is applicable for particle-associated species in general, although only total nitrate and sulfate can be measured, with considerable uncertainty as to the contribution by SO_2, HNO_3, and NO_x.

2. Strengths and Weaknesses

Snow sampling is simple and inexpensive to perform. The results provide flux measurements directly on a natural surface of interest. In cold climates and where there is sufficient snow, the method can be used to measure long-term total deposition.

Preconcentration of snow samples may be necessary to provide

sufficiently high concentrations for analysis of some species. Contamination by biological debris or soil dust may be a problem. The data may be difficult to interpret, due to complex in-snow transport processes. Species may be lost out of the top or bottom of the snowpack. Snow drift will obscure patterns of element accumulation.

3. Availability and Key Experiments

The methods involved are immediately applicable, but two to three years of research appear necessary to answer some questions that arise. Studies should be conducted to assess the consequences of ion migration through frozen and melting snow, meltwater percolation, and sublimation. Investigations of gas uptake by snow are also warranted. Deposition on snow needs to be compared with dry deposition estimated to snow by other techniques, such as aerodynamic surfaces and micrometeorological sampling.

H. Aerodynamically Designed Surfaces

An aerodynamically designed inert surface is exposed to the ambient atmosphere for a specified period of time. The device is positioned in an area with well-defined airflow characteristics, and at a location not significantly influenced by local soil resuspension. After a period of exposure, the deposited material is extracted and chemically analyzed to yield a deposition flux. The device is designed to have predictable collection performance, based on consideration of atmospheric conditions, surface conditions, and characteristics of the depositing species.

One example of this type of aerodynamic device, in the shape of a symmetric airfoil, has been developed. The device is Teflon-coated to provide a chemically inert surface. Preliminary results suggest that sedimentation dominates particle deposition onto this surface, and thus the total mass deposition is mostly influenced by the concentration of large particles in the atmosphere. The flux to the device is not greatly sensitive to windspeed or to atmospheric turbulence intensity, and hence the device can provide a measure of the size-integrated sedimentation flux as a reference to which deposition on natural vegetation can be compared.

1. Applicability

Space scale -- The device measures the deposition flux onto its active collection surface, approximately 100 cm^2. The extent to which the results can be extrapolated depends on the variability in the concentration and size distribution of large particles.

Time Scale -- The device can provide measurable fluxes for some species (e.g. sulfate) for exposures as short as several hours. Exposure could be several days or longer if desired.

Chemical Species -- $SO_4^=$, NO_3^-, metals, and alkaline particles (coarse fraction).

2. Strengths and Weaknesses

The device provides a direct measure of the sedimentation flux of large particles, which may be considered a lower limit to the total particulate deposition from the atmosphere. The technique is not adversely affected by the isokinetic sampling problems which inhibit accurate airborne concentration measurement. It is inexpensive to manufacture and to deploy in the field on a routine basis; extraction of deposited material for analysis is straightforward, and the device can be tailored to different uses. Siting characteristics are not as severe as for micrometeorological techniques.

The device needs protection from precipitation, using either a fixed rainshield or an automatically-deployed shielding system. Fluxes measured are not representative of the deposition onto more complicated natural surfaces. Birds, insects, and biological debris may cause problems of contamination. Resuspension of local soil and plant material may cause problems and must be controlled by siting the device sufficiently high above the local surface. Vapor adsorption onto deposited particles is a potential problem of unknown importance; appropriate studies are required.

3. Relevance to Modeling and Effects Research

When compared with fluxes determined by foliar extraction or throughfall, the influence of factors other than sedimentation of large particles onto foliage may be investigated assuming that coarse particle fluxes are comparable to each surface. Special experiments to test specific hypotheses relevant to modeling can be conducted. For example, the influence of SO_2 adsorption onto already-deposited large particles could be addressed by comparing aerodynamic surfaces with and without a layer of particles. The influence of large particles in neutralizing deposited acids could be investigated by similar controlled field experiments.

In concept, the surfaces could be fabricated from materials of interest to examine the effects of dry deposition on the "weathering" of materials (see section on Materials Effects).

Comparing deposition on the aerodynamic surface with that on natural vegetation may enhance our understanding of factors influencing fluxes to vegetation. For some atmospheric contaminants, species of vegetation, and meteorological conditions, deposition onto the aerodynamic surface may be similar to that onto vegetation.

4. Availability and Key Experiments

Prototype devices are presently available, however, wide deployment of the device should await the results of further performance tests in controlled conditions. These could be completed in 1 to 2 years.

- Controlled wind tunnel experiments are needed to determine deposition rates onto the device, as functions of particle characteristics, windspeed, and turbulence intensity.

- Field work is needed to investigate siting considerations and the influence of various designs of rainshields.

- Additional field and laboratory work is desirable to study several factors influencing deposition. These factors include the effect of surface roughness, the influence of dew, and conditions which promote resuspension.

I. Surface Analysis Methods for Material Effects

The surface analysis approaches proposed for studying dry deposition in ecosystems have analogues for materials effects research.

Surrogate surfaces. A classic materials experiment is the measurement of accumulated dry deposition to an exposed specimen of material of interest. As a result of recent developments, such specimens could be mounted in aerodynamically designed holders to control the effects of geometry on turbulent delivery to the surface.

Foliar leaching. An equivalent for materials is the rinsing of a building surface with distilled water, and subsequent chemical analysis of the runoff.

Throughfall. An equivalent is the collection of runoff from a surface as a result of a rainfall. The difference in ionic composition between the rainfall and the runoff is the result of reactions with the surface and of the removal of substances dry deposited to the surface.

Mass balance. It is possible to establish a mass balance over an urban area between the inputs of wet and dry deposition and the outputs as estimated from water quality measured at the outfalls of storm water runoff sewers.

Isotopes and radionuclides. Radioactive S-35 has been used in a number of experiments to study the rate of deposit to material surfaces in laboratory experiments. Stable S isotopes have also been used to evaluate the sources of sulfate found on materials surfaces.

1. Strengths and Weaknesses

Materials effects studies have several advantages over studies on living surfaces. The chemical reactions on the surface are much simpler and can be replicated with much greater ease in the laboratory. Analysis can be carried out on the actual collecting surface, either using wet chemistry or any of a wide range of instrumental methods. The geometry and orientation of the receptor surfaces is also much less complicated than for living surfaces.

Small specimens of material surfaces may not behave the same way toward dry deposition as do the larger scale materials being simulated. Scaling problems exist here similar to those discussed above for other surface analysis methods.

2. Availability and Key Experiments

Aerodynamic surfaces

The use of inert surfaces in aerodynamically-controlled mountings provide information on the role of large particles in the total dry deposition flux. Refinements to this technique could make it selective for other aspects of dry deposition. For instance, an aerodynamically rough inert surface would collect finer particles with greater efficiency. Reactive surfaces would investigate the role of individual chemical species in the deposition process. Covered versus uncovered collectors, or continuously wetted surfaces could also be used.

Controlled washing

Washing of materials surfaces under controlled conditions will yield information on surface reactions during rain events. Other uses of controlled washing that could be developed include the effect of surface geometry and composition on the runoff hydrology. Studies with water of known pH would further clarify reactions between wet deposition and dry deposition.

Rainfall runoff

An important topic for further research in this area is the effect of variation of the length of time between rain events on the subsequent surface leaching. The effect of varying rainfall intensity also needs more investigation.

Mass balances

A carefully designed long-term study of an urban area, where the materials inventory is known and the storm water system is well-characterized, should be done in order to evaluate the impacts of deposition and the outputs of reacted building materials.

Tracer studies -- stable isotopes and radionuclides

Labeled tracers in deposition should be applied to study the spatial variations in reactivity across a surface. Labeled surfaces should also be used, especially in the case of organic surfaces, to identify the most important reactions between deposition and surfaces.

J. Conclusions, and Recommendations Regarding Surface Sampling Methods

The capabilities of the methods considered in this section are summarized in Table 1. Consideration of the existing NAPAP program on dry deposition led to the following conclusions:

- More attention should be given to the needs of the biogeochemical cycling and plant and system effects researchers for atmosphere/surface exchange data; such needs are not always taken into account in the design of atmospheric chemistry and meteorology programs.

- Many models (such as RADM) address deposition on time and space scales that are inappropriate for the needs of the cycling/effects community (time scales are smaller than are necessary; space scales are larger than are useful).

- Current micrometeorological, concentration monitoring, and modeling techniques do not address many important atmospheric constituents (metals, cation nutrients, organics), nor complex/heterogeneous terrain sites.

To address these issues, a research program is needed with expanded attention to the following objectives:

- Develop or refine surface and atmospheric analysis methods for measurement of atmosphere/canopy exchange on scales useful for ecosystem and vegetation effects studies. Useful spatial scales are vegetation plot and watershed, while time scales are on the order of event to seasonal. The most promising surface methods appear to include inert surfaces for coarse particles and foliar extraction for total particles to individual surfaces, throughfall for total particles and potentially some vapors and gases to tree canopies, and watershed mass balance for dry deposition to the complete landscape (See Table 2).

- Combine these methods to measure dry deposition at carefully selected, generally representative, sites on the scale of plots to small watersheds in conjunction with the most promising micrometeorological and inferential (or concentration monitoring) methods. The objectives of these experiments are (1) to compare independently measured fluxes at single points to determine the relative contribution of fine and coarse particles and vapors and gases to atmosphere/canopy exchange (dry deposition in particular) and to determine the magnitude and sources of error of these measurements; and (2) to develop scaling parameters for selected particles and vapors to go from point measurements (both surface and aerometric) to appropriately larger scales.

- Develop a model or models for estimation of atmosphere/canopy exchange at a range of locations based on on-site, routine meteorological, air chemistry, and surface measurements.

Several key experiments designed to address some uncertainties in assumptions of various surface analysis methods are outlined in the above descriptors of each method.

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Table 2

Relevance of surface analysis methods to quantification of dry deposition to environmental surfaces and other needs of NAPAP. The methods were evaluated by the group on a relative scale (high, medium, low) for their potential to contribute useful information in the above areas in a two to three year time frame. Some methods are more applicable to certain chemical species, while others require testing of key assumptions prior to application on large spatial scales (see discussions in the text).

Method	Regional-Scale Model Evaluation	Effects on			Network Monitoring
		Plants	Materials	Ecosystems	
Aerodynamic Surface	L	M	H	M	H
Foliar Extraction	L	M	H	M	M
Throughfall	M	H	H	H	M
Watershed Mass Balance	H	M	M	H	L
Isotopes	L	M	M	M	L
Snow Sampling	M	L	L	M	M

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VI. ATMOSPHERIC FLUX METHODS

A. Introduction

Atmospheric techniques to measure dry deposition have evolved over the past few years, but the types of techniques are still quite similar to those discussed in the preceding dry deposition workshop in 1979. Here, we review seven of the methods: tower-based eddy correlation, vertical gradient, eddy correlation from aircraft, aerometric mass balance, multiple artificial tracers, eddy accumulation, and variance. In 1979, these were viewed as research techniques, and it was the consensus that the vertical gradient, eddy accumulation, and variance approaches had the highest potential for development for routine monitoring, among all techniques addressed at the workshop. Although none of these methods have yet been implemented on a truly routine basis, some of the tower-based methods are used periodically at the three CORE research stations, and form the basis for parameterizations to be applied at other sites where less intensive, indirect measurements are made so that deposition velocities can be derived. Also, tower-based eddy correlation and gradient methods, together with laboratory studies and investigations of plant physiology, have provided the major sources of information on dry deposition in regional-scale numerical models of transport and deposition.

The main charge to this working group was to review the seven atmospheric flux measurement techniques with regard to

-- the accuracy and precision achievable in the field,

-- the space and time scales addressed,

-- the chemical elements and species that can be measured,

-- the feasibility of developing routine, direct measurement methods,

-- the amount of time for development needed before useful results can be obtained, and

-- the relative cost-effectiveness of the approach.

In addition, some special issues were identified by the working group. One issue that was considered important is the strong need for additional supportive data, mainly to provide detailed surface information. However, this was not addressed directly by this working group, but is implicit in the suggestions (given later) for future collaborative experiments involving methods examined by the other working groups at this workshop. Other issues include the effects of flow over complex terrain, rapid in-air chemical reactions, edge effects, and plume impaction.

With the strengths and weaknesses of each approach in mind, the group deliberated on future research directions relevant to NAPAP goals. For a framework, it was assumed that 5 to 10 dry deposition stations would be selected where the atmospheric flux measurement techniques would be applied and that these would produce a considerable amount of reliable dry deposition data within two years. It was assumed that intensive, totally independent methods such as discussed by the other working groups at this workshop would be implemented simultaneously. Of course, the applicability of each atmospheric flux technique depends on the purpose of the measurements: routine network operation for study of terrestrial effects, routine network operation for the detection of time trends and spatial differences, and diagnostic evaluation of regional models of transport and deposition. Since none of the methods were considered very suitable for studies of long-term (10 years or more) dry deposition, this application was not considered.

The following discussion summarizes each atmospheric flux measurement technique. Following this discussion of the individual methods, the most important considerations are brought together in a review of strengths, weaknesses, and applicabilities. Finally, suggestions for new research directions are outlined at the end of this section.

B. Tower-Based Eddy Correlation

Tower-based eddy correlation techniques can measure the turbulent flux of substances across a plane at the height of the sensors, if a fast, robust sensor is available for that substance. If the purpose of these measurements is to characterize the atmosphere-surface exchange, then these measurements need to be made at a height above the surface of interest, typically 5-10 m, where a well developed boundary layer exists. The nature of turbulent processes requires surface uniformity in the upwind direction, typically for 500 m, since the technique "sees" this expanse. If canopy roughness and unstable meteorological conditions enhance turbulent mixing, the classical micrometeorological fetch requirements can sometimes be relaxed. On the other hand, if deposition velocities are small, then fetch (and stationarity) requirements can become more demanding. Coordinate

rotation may be required since eddy correlation only measures turbulent exchange across the streamline flow which is not always perpendicular to the anemometer vertical orientation.

The measurement of flux to the surface by eddy correlation is necessarily limited to chemical species which have no sources or sinks between the point of measurement and the surface. In addition, the chemical sensor response time must be sufficiently fast to ensure that all time scales contributing to the turbulent exchange process are included in the measurement. Good flux estimates can usually be made with time responses as large as one second in most conditions if small adjustments are computed to account for the loss of high-frequency contributions to the turbulent flux. Chemically pure specification of the concentration signal is desired, otherwise contaminant flux measurements should be made coincident to the flux measurement. Detrending of concentration variation via numerical filters can relax stationarity requirement associated with classical micrometeorological measurements. Measurement of delay times due to separation of chemical sensors and a vertical anemometer is needed for correcting covariance cross product formation; excessive delay times and response times can lead to flux underestimation. The applicability of the eddy flux measurement technique for pollutant exchange should be predicated on the ability to yield accurate measurements of eddy fluxes of heat, as can be tested by comparison against net radiation and heat storage values measured independently.

1. Applicability

Space scale -- The technique normally "sees" a wedge of the surface extending for a distance depending on surface roughness and the height of measurement, but typically about 500 m upwind of the measurement location, and typically 30 degrees wide (depending on the atmospheric conditions).

Time scale -- Measurements are normally obtained using fast response sensors (1 Hz or faster), from which fluxes are computed over averaging times usually from 15 to 60 minutes.

Chemical species -- The method is applicable only for species that currently have sensors with fast enough response times: O_3, $SO_4^=$, SO_2, NO, and NO_2. Some of these sensors suffer from interference from other trace gases, such as CO_2, H_2O, and potentially, trace organic species.

2. Strengths and Weaknesses

The accuracy of eddy-correlation flux estimates is known to be quite high in ideal conditions, largely as a result of experiments in which heat and water vapor fluxes have been measured and compared to results from surface energy budgets and weighing lysimeters. Levels of uncertainty of the order of 10% have been achieved for heat and water vapor over periods of several hours. An assessment of the uncertainty associated with measurements of the eddy fluxes of

quantities other than H_2O (and CO_2) has not been carried out by comparison to other techniques applied independently. Sources of error unique to chemical eddy flux measurements are of concern; these include the effects of advection from strong sources, flow distortion over nonuniform terrain, and chemical interference by other trace species. Comparison experiments involving independent adjacent eddy correlation systems, sometimes at different heights, indicate uncertainties of about 30% for sulfur and ozone, for half-hour average fluxes.

The precision of eddy correlation flux measurements has been well documented. Natural geophysical variability usually limits the precision of flux measurements made at a height of several meters to 10 to 30%, depending on the wind speed and atmospheric stability, over a 30 minute period. Precision of eddy fluxes improves in proportion to the inverse of the square root of the averaging time. There are special problems, however, that must be addressed with even the best of modern trace gas and particle sensors. Foremost are the effects of sensor noise, and the consequences of poor detection statistics (especially important in the case of particle fluxes). Published analyses have shown that these effects can greatly increase the variability (measured as a standard deviation) of flux estimates.

Tower based eddy correlation has difficulty addressing edge effects, or transport in complex terrain where advective affects are also present.

3. Relevance to Modeling and Effects Research

Eddy correlation from towers requires an intense effort that can provide the basis for parameterization of air-surface exchange. Although the technique is not suitable for long-term continuous application, it can be applied periodically to "calibrate" methods less demanding in terms of manpower and skills.

4. Availability and Key Experiments

Several teams of researchers now have developed independent capabilities to measure eddy fluxes of trace chemical species. Additional fast-response sensors would be necessary to permit work at more than three or four sites.

Some additional requirements that should be included when considering the use of eddy-correlation technique for a large number of sites are moderate expenditure for rapid analog to digital signal conversion and computing capabilities needed for on-line processing. Independent concentration measurement are useful for deposition velocity determination especially in low concentration regimes. Use of eddy correlation over complex terrain would require considerable research.

C. Vertical Gradient Measurements

The gradient technique can be used to estimate the dry deposition

of several rapidly depositing species to relatively short vegetation. It has the advantage that it can measure fluxes of those species whose concentrations can only be measured using slow techniques such as filterpacks or real-time continuous monitors in multi-level sampling arrangements. Unfortunately, the technique places extreme requirements on the precision of the measurement system, since small differences in concentration must be used to estimate the flux.

1. Applicability

The spatial and temporal scales are the same as for eddy correlation from towers. Gradient measurements have already been used to measure dry deposition rates of ozone, sulfur dioxide, nitric acid vapor, and a few other species whose surface resistances are small.

2. Strengths and Weaknesses

The precision required for making flux estimates from gradients is high; for the most rapidly depositing species, 1% to 2% is necessary for the concentration measurements at each level to obtain a 10% to 20% precision on the differences. (For slowly depositing species, the differences are too small to measure with adequate precision, so gradient-based deposition estimates are likely to be susceptible to error.) When one adds in the uncertainties for the supporting measurements of sensible heat flux and gradients, accuracies in the range of 30 to 50% seem to be the limits.

Another major uncertainty must also be considered. In order to relate the gradients to fluxes, one must estimate an eddy diffusivity for the species in question. In practice this is usually done by assuming that the transport of sensible heat and mass are analogous. While this analogy is apparently quite reasonable over low vegetation and smooth surfaces, it is unlikely to represent reality very well over deep canopies. Before we can use gradient methods to measure dry deposition rates to forests, there must therefore be development work carried out on ways to convert the measured gradients into flux estimates without significant error. Some of the necessary work is underway.

3. Relevance to Modeling and Effects Research

The revelance is the same as for eddy correlation from towers except that long-term measurements may be possible over uniform areas with short surface elements. This would substantially bolster efforts for effects research and model evaluation.

4. Availability and Key Experiments

The gradient method can be used currently to estimate the dry deposition of several subatances that are important to NAPAP. Because of interpretation difficulties, however, it is not clear whether or not gradient techniques can be used to measure the deposition of acids and precursors to forests within the next two years. For long-term measurements, a considerable investment in technology would be necessary.

D. Eddy Correlation From Aircraft (and small-scale aerometric mass budgets)

Aircraft flux measurements at several levels within the boundary layer can be used to measure the vertical profile of the flux, which, when extrapolated to the surface, gives the surface exchange, and when differentiated with respect to height, gives the flux divergence. The flux divergence is balanced by the time rate of change of mean concentration and by mean advection (if the flight pattern is not advected by the mean wind), which can also be measured with the aircraft, and the chemical source or sink in the atmosphere, which can be estimated as a residual term. This approach can be particularly useful for evaluating the accuracy of the vertical flux measurements of a conserved species. Aircraft mean concentration and flux measurements can also be used in an appropriately designed flight pattern to evaluate mass budget of a particular species.

1. Applicability

Space scale -- The spatial scales are fairly large, since a minimum flight path of approximately 20 km is needed. A folded path could be used to average over areas perhaps as small as 5 km on a side.

Time scale -- Temporal scales are small, on the order of 5 min, commensurate with aircraft speed. Maximum averaging time is typically 3 hr, depending on type of aircraft and amount of ferry time.

Chemical species -- Proven systems exist for O_3, H_2O, CO_2, heat, and momentum. Further development is needed for sulfur and nitrogen species.

2. Strengths and Weaknesses

Compared to tower-based measurements, aircraft have the advantage of being able to measure rapidly both horizontal and vertical variations of mean concentration and flux. Also measurements are feasible in remote areas that may be nearly inaccessible from the ground (e.g., oceans, forests, swamps, tundra, etc.). Flux measurements over inhomogeneous terrain can be obtained, as long as the scale of the inhomogeneities is small compared to the length of the flight path. On the other hand, measurements of continuous temporal variations in means and fluxes are difficult because of the limited flight duration, and measurements within about 30 m of the surface are precluded for safety reasons. These limitations can usually be overcome with complementary tower-based measurements. Because the aircraft flies at speeds about an order of magnitude faster than the typical mean wind speed, the maximum frequency required for flux measurements is also increased over that required for tower-based measurements. This means that the desired frequency response is about 10 Hz, although a maximum frequency of 1 Hz could still provide useful flux measurements. Furthermore, flow-related errors may be larger than for towers.

The overall accuracy of the aircraft flux measurements is similar

to that of tower-based measurements. Since the aircraft usually flies five to ten times faster than the mean wind speed, geophysical variability is reduced accordingly. At the same time, the magnitudes of concentration fluctuations encountered by aircraft are typically lower than experienced using towers (a consequence of the greater height of measurement), and hence aircraft measurements may be more affected by sensor noise.

The greatest limitation to widespread use of aircraft for surface exchange measurements is the lack of proven sensor systems that can meet the necessary noise and time-response specifications. At present, at least two NCAR and one NOAA aircraft are equipped with flux measuring systems. Analyzed flux data can be made available typically within about six months after an experiment.

There is the possibility of carrying out atmospheric box budgets with slow-response chemical sensors over scales of 80 to 100 km. It is not certain, however, that accurate deposition estimates can be obtained even with highly intensive experiments utilizing multiple aircraft, surface measurement sites, and vertical soundings.

E. Aerometric Mass Balance Studies

Aerometric mass balances are based on measuring the horizontal fluxes into and out of a volume of air. Also, the fluxes across the top level of the volume, internal sources, and chemical reaction rates (if relevant) should be measured, estimated, or known to be negligible. Dry deposition is found as a remainder or difference term. Regional to continental scale mass balance experiments require numerous aircraft cross sections reaching to relatively high altitudes. This approach generally involves moderate to high aircraft costs, and sampling instrumentation capable of detecting the low concentrations typically found aloft (for example, a few ppbv or less of sulfur dioxide).

1. Applicability

Space scale -- Distances of at least 100 km are usually needed to detect changes in concentration due to dry deposition.

Time scale -- Effective averaging times are at least the time of transit of wind across the area of interest: a minimum of about two hours for distances of 100 km. For regional to continental scales, averaging for several days may be required.

Chemical species -- Slowing reactive species that are present in concentrations of at least an order of magnitude above instrumentation detection limits are most desirable. Sulfur dioxide seems the best candidate if instrumentation can be made sufficiently sensitive and accurate.

2. Strengths and Weaknesses

If measurements are made within tens of kilometers of point sources of pollution, the sampling demands in terms of number of flight

altitudes and horizontal spatial coverage become especially great. On the whole, there is as yet no convincing evidence that, on a large regional scale, it is possible to achieve an accuracy of better than our present mass-balance estimate of dry deposition of perhaps about 100%. This accuracy estimate is consistent with that made in the past by scientists planning the MATEX experiment for EPRI. Furthermore, there is an apparent inherent limit on accuracy in that the estimated uncertainty in flux estimates is of the same order as the estimated dry deposition over eastern North America. On the whole, the mass balance approach does not now appear to be a cost effective way of obtaining regional average dry deposition; it does not pretend to provide detailed estimates of dry deposition on smaller scales. Despite this, the use of aircraft cross-sectional flights remains the most effective, although costly, means for estimating horizontal fluxes across boundaries between large areas.

3. Relevance to Modeling and Effects Research

The mass balance technique is most suitable for studies of dry deposition over rather large areas and this is most relevant to testing the spatially-integrated outputs of deposition models.

4. Availability and Key Experiments

The NAPAP now supports Western Atlantic Ocean Experiment (WATOX), part of whose objective is the determination of fluxes of sulfur and nitrogen compounds into the North Atlantic Ocean. Several aircraft flights taking cross-sectional samples have already been undertaken. A number of scientific results have been published including estimates of horizontal exit fluxes, from which one may calculate through mass balance that the dry deposition of sulfur for eastern North America is of the same order as wet deposition. Future flux measurements will be based on very limited aircraft sampling to altitudes of about 5 km altitude. Application to smaller areas is perhaps best accomplished in conjunction with eddy correlation from aircraft, as discussed in Section D.

F. Multiple, Artificial Tracers

In concept, the dry deposition velocity of an atmospheric pollutant can be determined by releasing the material from a known source and measuring the loss of material from the plume as a function of downwind distance. In practice, problems with spatial sampling make a simple mass budget measurement very difficult. Addition of a second, nondepositing tracer, however, may greatly improve the accuracy of the deposition estimate.

For horizontally homogeneous conditions, a dual-tracer, surface depletion technique for determining deposition velocities has been demonstrated successfully. The sampling problem is alleviated using only surface sampling, which can be implemented much less expensively than the elevated sampling required by a mass budget. Deposition velocities of 1 to 4 cm s^{-1} were determined for a ZnS tracer at distances of 1.6 to 3.2 km. The technique requires adequate deposition

to produce a measurable horizontal gradient in ground level concentrations of the low-level releases under stable atmospheric conditions. Extension of the technique to horizontally heterogeneous conditions would require theoretical analysis and exploratory field experiments.

1. Applicability

Space scale -- Depending on experimental design, 100 m to 100 km are appropriate scales of travel distance.

Time scale -- One hour to nearly one day is appropriate.

Chemical species -- Those on large particles are suitable. Other possibilities include quickly depositing substances (e.g., HNO_3 and HF), as well as specially prepared compounds of sulfur and nitrogen tagged with minor isotopes.

2. Strengths and Weaknesses

The accuracy of the deposition velocity derived from these techniques is principally a function of the accuracy to which the concentration can be measured and is inversely proportional to the fractional tracer loss. Hence the accuracy of any given field experiment is critically dependent on the specific experimental design. Tests conducted so far have been limited to conditions of stable atmospheric stratification.

3. Relevance to Modeling and Effects Research

This approach is most practical to devote to study of details of dry deposition processes, thus leading to parameterizations useful in both modeling and effects research. It is suitable for intensive studies but not routine application.

4. Availability and Key Experiments

Successful use of multiple, artificial tracers for studies of sulfur and nitrogen deposition will require further development and exploratory studies, especially if horizontally nonuniform conditions are considered.

Dual tracers could be used over heterogeneous terrain by assuming that, under vertically well-mixed conditions, the fractional loss from the plume is equal to the depositing to nondepositing tracer concentration ratio. However, Horst (unpublished manuscript, 1986) has shown that travel distances of 50 to 200 km are required for (1) measurable deposition to occur, (2) the plume to be well mixed, and (3) the deposition to be quasi-uniformly distributed over the downwind extent of the experimental area. For a wind speed of 3 m s^{-1}, this would require the experiment to last for 5 to 18 hrs. It is unlikely that this would be a stationary period and a depositing tracer has not been identified that could be released in sufficient quantities to be detected at these distances. Tracer development and exploratory field experiments are required.

Experiments conducted over shorter distances (approximately 10 km) of non-uniform terrain have certain limitations. For example, the assumption of a well-mixed plume usually cannot be made, as explained above. Development of different types of experimental strategies, such as the use of line sources and extensive vertical sampling, would be necessary. If sound strategies can be developed, some special cases could be investigated, e.g., removal of airborne substances by rows of trees perpendicular to the wind. To obtain a sufficiently large difference between depositing and nondepositing tracers after only about 10 km of travel, the deposition velocity of the depositing tracer should be large. In this case, lower limits may be placed on removal rates (deposition velocities) from shorter-range, more feasible multiple-tracer experiments.

One dual-tracer technique, which is currently unexplored, is the use of diffusion-deposition models to interpret the experimental results. The basic idea is to use the nondepositing tracer measurements to calibrate the transport and diffusion model, and then use the depositing tracer measurements and the deposition model to infer a deposition velocity. The advantage is that much shorter travel distances are feasible because the concentration ratios can be measured under stable atmospheric conditions and close to the surface.

G. Eddy Accumulation

Eddy accumulation has the potential for replacing fast-response chemical sensors such as are used in eddy correlation. Fast-response vertical velocity signals are used to control sampling rates of two integrating samplers. One is associated with updrafts and the other with downdrafts. The flux is obtained from the difference in mass of the trace substance for the two samplers. The system requires that the usual micrometeorological fetch be satisfied and the vertical velocity sensor be well aligned and the signal passed through a high-pass filter. If the vertical wind sensor cannot be well aligned at all times, a real-time coordinate rotation, which requires fast response horizontal wind measurements, is needed. The electromechanical sampling system's flowrate must accurately track vertical wind speed fluctuations. The analytical precision for the pollutant mass collected by the samplers must be less than ±1% to achieve a best estimate of accuracy of flux less than ±20%.

1. Applicability

Space scale -- The areas sampled are the same as for other tower based micrometeorological methods such as eddy correlation and gradient techniques.

Time scale -- The basic period for which this method is designed is approximately one week, but can be as short as other micrometeorological methods if sufficient material is collected for chemical analysis.

Chemical species -- The method is applicable to trace gases and particles with diameter less than one micrometer.

2. Strengths and Weaknesses

The advantages are that (1) direct measurements of vertical flux averaged for as long as one week can be made, (2) one device may be used to obtain fluxes for many substances, (3) fast-response chemical sensors are not needed, and (4) composition analysis of particulate material can be carried out.

The disadvantages are that (1) particular care must be taken with vertical alignment of the vertical wind sensor if a real-time computation of coordinate rotation is not performed, (2) as a micrometeorological method, the usual fetch requirements can be demanding for flux monitoring sites, (3) strict precision of less than 1% for chemical analyses of samples is needed to achieve best estimate of accuracy of ±20%, (4) highly accurate flow control is needed, and (5) inlet efficiency is expected to be variable for particle sampling, especially for diameters greater than about one micrometer.

The accuracy obtainable with this method is in principle as good as eddy correlation, but may be further limited by factors associated with chemical analyses and with the control of the sampling rates. A reasonable expectation is that accuracies of ±20 to 50% are achievable for substances such as H_2O, SO_2, HNO_3, and particulate nitrate.

3. Relevance to Modeling and Effects Research

Eddy accumulation can be used for a wide range of applications. It conceivably could be more effective than other micrometeorological approaches for intensive experiments, and extend such capabilities for direct flux measurement on a routine basis.

4. Availability and Key Experiments

We are aware of only two research groups that have research eddy accumulator prototypes. These are AES-Environment Canada and ASRL-Environmental Protection Agency. The performance of these systems is still under review, and the current versions are not documented. The potential advantages of this technique warrant further intensified development among independent investigation teams. It is a reasonable expectation that a successful version can be demonstrated within two years that has "best achievable accuracy" of ±20 to 50% for water vapor, sulfur dioxide, and nitric acid/particulate nitrate.

H. Variance Technique

The variance technique can produce estimates of the magnitudes of the vertical fluxes of substances whose variance of concentration fluctuations can be measured at a height of several meters at a site where friction velocity and atmospheric stability are estimated. The latter quantities are routinely derived from measurements made in the NOAA trial measurement network, and can be derived from measurements made in the EPA dry deposition monitoring network. The parameterizations necessary to relate standard deviations, friction velocity, and atmospheric stability are available in the scientific

literature. There are several other variance approaches that are feasible, such as use of a modified Bowen ratio based on ratios of standard deviations rather than vertical gradients.

1. Applicability

Space scale -- Areas covered by tower based micrometeorological methods are addressed.

Time scale -- Estimates of fluxes are made for time periods of about one hour.

Chemical species -- Included are those species for which fast-response chemical sensors are available: sulfur dioxide, sub-micrometer sulfate, nitrogen dioxide, and ozone.

2. Strengths and Weaknesses

The major advantages of this approach are that fast-response wind sensors, which can be difficult to operate on a routine basis, are not needed, and commercial sensors can be used for the required chemical measurements. However, suitable sensors are available for only a few chemical species and are relatively expensive, in the range of $5,000 to $10,000 for each substance at each measurement site. Furthermore, some of these sensors require frequent attention, preferably at least three times a week when operated continuously.

A microprocessor to perform the necessary calculations is needed at each site. Fluxes computed via the variance technique are susceptable to overestimation caused by nonatmospheric "noise" in the chemical sensor. Also, the sign (direction) of the flux is not provided directly. Some of these deficiencies are being addressed by current research.

Short-term flux estimates produced are probably no better than ±50% for the local surface; longer term averages, such as one week, should have uncertainties in the range of 20 to 30%, although systematic errors or offsets are difficult to determine.

3. Relevance to Modeling and Effects Research

The variance approach has been used to date primarily as a supplementary micrometeorological method during intensive experiments. It is a valuable tool to extend and help interpret results from eddy correlation and gradient techniques. Also, the variance method could be used for routine flux measurement to an extent determined by the resources available to obtain fast-response chemical sensors.

4. Availability and Key Experiments

The variance technique can be implemented immediately. Documentation for this approach is not complete. A preliminary, informal report has been produced and the scientific basis for the approach has been examined in peer-reviewed scientific literature. The

current NAPAP schedule calls for a complete evaluation by the middle of 1986. One of the difficulties being addressed by current research is that the necessary fast-response chemical sensors often are "noisy" at the frequencies associated with flux-carrying eddies, from 0.1 to 1.0 Hz. In some cases, selective electronic filtering can isolate partial variances uncontaminated by nonatmospheric noise. One method that has been developed is to isolate atmospheric fluctuations via use of covariance with at least two other scalar quantities that are noise-free. This can be readily implemented, for example, with sulfur sensors by use of covariances with temperature and ozone fluctuations.

I. Summary of Strengths, Weaknesses and Applicability

The tower-based approaches that are micrometeorological in nature include eddy correlation, gradient, and variance techniques. These deal with time scales of 0.5 to 4.0 hr and space scales of 0.1 to 1.0 km. The techniques measure the vertical flux above the surface, and are known to be highly successful above uniform terrain. Achievable accuracy and precisions are on the order of 20% over a period of several hours, provided sufficiently accurate sensors are used. So far, a thorough assessment of accuracy of the flux measurements for ozone and sulfur and nitrogen compounds has not been accomplished by comparison to truly independent measurements. The measurement techniques are in practice and are immediately available. For the eddy correlation and variance approaches, the fluxes measured are limited to those chemical species for which fast response sensors are available: SO_2, O_3, NO, NO_2, and sub-micrometer SO_4. The number of widely scattered sites for eddy correlation that could be deployed is limited to less than ten because of the limited availability of researchers to employ the highly specialized techniques necessary. For all three of these approaches, the costs are fairly high, since these are essentially research-grade operations and, for the techniques that require fast-response sensors, the costs of instrumentation are substantial.

Eddy accumulation is an application of eddy correlation potentially allowing flux measurements over a period on the order of a week long, in a routine monitoring mode. Furthermore, the fluxes that can be measured by eddy accumulation (and the gradient method) are not limited to the chemical species for which fast-response sensors are available. While the eddy-accumulation method has a very high potential for measuring fluxes routinely, development of the technique is not complete and might not be available for deployment at a large number of sites within two years.

The tower-based methods described above measure the vertical flux above the surface, which is not necessarily the same as the flux at the air-surface interface if rapid chemical reactions or advection from upwind strong sources cause a change of flux with height. Furthermore, these tower-based measurements only give the net flux to the bulk surface over horizontal upwind distances of 0.1 to 1 km. Although comparisons of fluxes of different chemical species, water vapor, heat,

and momentum often can give substantial information on the vertical and horizontal distribution of uptake locations for airborne substances, the information is usually inferior to that which might be obtained by direct sampling of surface properties or deposition. Over horizontally nonuniform surfaces, the tower-based methods do not necessarily provide representative samples of the flux; the effects of large aerodynamic obstacles upwind, local variations in uptake such as near edges of deep canopies, and hilly terrain are very difficult to address with the traditional tower-based measurements described here.

Measurements of vertical fluxes by eddy correlation from aircraft can rapidly integrate fluxes over fairly large areas, with flight paths on the order of 20 km long at heights of 30 to 150 m. Only two to four facilities are available for such measurements at the present time. They provides a means of integrating fluxes over nonuniform terrain, provided the characteristic length scale of the surface nonhomogeneities are small compared to the flight path. Aside from this capability to integrate and the ability to take measurements over remote areas difficult to reach on the surface, aircraft eddy correlation shares many of the advantages and disadvantages of tower-based eddy correlation. Of course, the flight time is limited by cost and the inability to take measurements in certain conditions (especially at night). For such reasons, flux measurements from aircraft are best suited for studies in which the deposition velocities averaged over fairly large areas are needed, and trends of deposition velocity with time are best accomplished by simultaneous, longer-running flux measurements from towers that can resolve fluxes in short time intervals for comparison to the aircraft data.

Aerometric mass budgets and use of multiple artificial tracers are attractive in part because they are not based on micrometeorological relationships and thus offer independent approaches. A number of strategies for implementation of these approaches have been suggested, but few have stood up to detailed examination. Feasibility tests are needed to determine precision and accuracy. Aerometric mass budgets over continental areas seem to yield dry deposition velocity estimates for sulfur to within about a factor of two. Smaller scale mass budgets have not been attempted recently; attempts in the 1970's were unsuccessful. Several approaches with multiple artificial tracers have been suggested and the most feasible seem to be for substances with large deposition velocities over uniform terrain. Measurements of rapidly depositing tracers for distances of up to 10 km from line sources might provide a means of measuring deposition over nonuniform terrain if extensive vertical sampling based at the surface can be accomplished. As with flux measurements from aircraft, these methods do not lend themselves to routine monitoring but to intensive studies in which the deposition velocities over large areas are desired.

The applicability of atmospheric flux measurement techniques to some selected needs of NAPAP are summarized in Table 3. Here, a rating of 5 indicates that the method can provide substantial amounts of the data needed within a two year time period, is proven feasible and reasonably accurate (±30%), and can be implemented with low cost. A rating of zero implies that the method is not applicable. For this

exercise, it was assumed that the main need of routine network studies of aquatic effects is to provide seasonal averages of sulfur fluxes. For terrestrial effects, the purpose assumed is to obtain weekly averages of fluxes of ozone and sulfur and nitrogen compounds over periods of several months. For diagnostic model evaluation studies, the need targeted is to measure deposition velocities of key airborne substances, primarily gaseous and particulate sulfur, averaged over areas of at least 20 km by 20 km, or provide needed supportive measurements from towers at the surface. The highest number in the table refers to the use of aircraft to provide data for testing diagnostic model predictions. In this context, aircraft offer a unique capability for spatial averaging, although there are very few chemical species that can be addressed and successful application over complex terrain has not yet been demonstrated.

Table 3. Current applicability of atmospheric flux methods to measure dry deposition to environmental surfaces. Ratings are on a scale of 0 to 5, with 5 a high score indicating ability to produce substantial, reliable results within a two year period.

	Routine Network, Aquatic Effects	Routine Network, Terrestrial Effects	Diagnostic Model Evaluation Studies
Tower-based eddy correlation	1	3	3
Vertical gradient measurements	2	2	3
Eddy correlation from aircraft	1	2	4
Aerometric mass budgets			
regional	0	0	1
50 to 100 km	0	0	2
Multiple, artificial tracers			
approx. 100 km	0	0	1
approx. 10 km	0	0	3
Eddy accumulation	2	3	2
Variance technique	1	2	2

J. Conclusions, and Recommendations for Research

Some opinions on current dry deposition research arose during discussions that were shared by most of the working group members. For

one, continuation of the CORE station program was considered vital, especially in regard to interpreting results obtained with the routine monitoring network being established. There was some concern that interpretation of monitoring data on concentrations and local micrometeorological and surface conditions must be carefully done by experts but it was not clear to all that the link with the experts has been formally established. Many of the participants felt that it was necessary to distinguish between atmospherically stable and unstable conditions at the monitoring sites, in order to interpret the raw data correctly. Also, the suggestion was made that two levels of filter pack measurements should be considered, so that the gradient technique could be attempted and thus dry deposition computed more directly.

It was recognized that many of the micrometeorological approaches do not provide information on some of the substances important in studying ecosystem effects. While fluxes of O_3, SO_2, sub-micrometer $SO_4^=$, and some nitrogen compounds can be measured by some of the micrometeorological methods, estimates of dry deposition of metals, cation nutrients, and organics are usually not provided. For these, the eddy accumulation and gradient (modified Bowen ratio) method hold the most promise and should be pursued vigorously.

It was recognized that modeling of dry deposition occurs on two levels: one for regional-scale numerical models of transport and dispersion, and one for site-specific effects studies. For the regional modeling, research should be directed towards scaling up the findings at individual locations. This falls under the category of diagnostic model evaluation studies. For this, measurements of fluxes integrated over large areas are needed and must be compared to the sum of deposition computed on the basis of summing estimates of fluxes to individual surfaces underneath. It was suggested that eddy correlation from aircraft could be implemented most effectively for this purpose, provided suitable fast-response sensors are developed quickly. Measurements of fluxes above homogeneous surfaces can be accomplished with the tower-based micrometeorological techniques. Alternative or supplemental to the flux measurements from aircraft are aerometric mass budgets and multiple, artificial tracer studies. Both of these approaches need considerable development before reliable application; studies of processes of deposition using rapidly depositing tracers for special cases of nonuniform terrain were considered feasible.

The other level of modeling deals with describing dry deposition processes at individual surface elements and summing up the contributions to yield the total deposition at specific sites. This level of modeling seems most appropriate in support of the terrestrial and aquatic effects studies that are needed, and should perhaps be the emphasis for future NAPAP research on dry deposition. The micrometeorological methods provide an estimate of the total dry deposition from the atmosphere and should be used to test the ability to combine results obtained from studies of individual surface components. In such work, it is essential to link research involving studies on atmospheric flux measurements with surface analysis methods, modeling, and controlled experiments. This means that atmospheric

scientists, geochemists, and biologists must work together closely in field experiments.

The group strongly recommended a series of comparison experiments in which a wide variety of techniques are employed simultaneously over the same areas. Methods include atmospheric flux approaches, surface analysis techniques, and applications of models utilizing both laboratory experiments and measurements of surface properties at the field sites. At least the following type of surfaces should be considered:

- A site with uniform surface characteristics amenable to reliable application of as many different techniques as possible. This is needed to build confidence in available techniques and to test new methods.

- Sites with varying degrees of surface nonuniformity, in gradations of complexity, to isolate difficulties associated with edge effects, hills, etc.

- Calibrated watersheds, which should coincide with enhanced monitoring stations or dry deposition core sites. It would be useful to have one site particularly well equipped so that researchers from diverse groups would have access to the necessary logistical support and field facilities.

For the micrometeorological measurements, it seems necessary to begin an immediate, intensive program to develop the necessary fast-response chemical sensors needed, and to enhance current efforts to develop atmospheric measurement technique that do not require fast-response sensors.

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VII. SITING STRATEGIES FOR MONITORING

A. Introduction

The Siting Strategies Working Group was assigned the task of developing plans for siting of dry deposition/concentration monitors in support of NAPAP objectives. The group spent some time in identifying key issues and better defining and limiting the group's area of responsibility. The decision was made to restrict discussion to developing siting strategies for routine monitoring networks. Site selection for intensively managed research areas should be left to the individual project directors. For example, additional CORE sites should be selected by those performing the "benchmarking" studies, and the forest effects researchers should select sites most appropriate for their needs.

Whether to refer to the routine sampling sites as "dry deposition" or "concentration monitoring" network sites was discussed. It was understood that the deposition velocity (V_d) cannot be estimated at all sites nor will it be possible to estimate V_d for some species. Even with these limitations the group felt that the dry deposition name should be retained. This implies that whenever the network is discussed, it must be specified as to whether flux or concentration is being reported.

The group recognized the limitation in determining the deposition velocities for many species, ground covers, and terrains. Thus, it is strongly recommended that additional CORE sites be deployed to address these shortcomings.

B. Data Users

There are at least five user groups within NAPAP that require routine monitoring data -- atmospheric modelers, trends analysts, and the terrestrial, aquatic, and materials effects researchers. Because of differences in spatial and temporal requirements, no single network can accommodate all needs. Thus, each user group will require its own network. Where possible, multiple needs will be accommodated at each site. By using the most demanding need (i.e., continuous monitoring) at some sites, the data can be "averaged up" to meet other requirements. As a result, some sites will meet the needs of more than one user group. After extended discussion on how best to allocate the limited resources to obtain the most important information first, the group assigned a priority to each of the user groups. Modelers' needs were assigned the highest priority followed by trends, terrestrial, aquatic, and materials effects.

Several factors were considered in placing the model evaluation needs first. Given the probability that a large dry deposition network will have a limited life time, an evaluated model will provide a tool that can be used long after the network has been discontinued. Near term benefits of an evaluated model includes being able to provide to effects researchers some bounds of exposure that can be anticipated. The data base obtained during the model evaluation exercise can also be used to establish wet/dry deposition ratios. If these ratios remain constant over time, then dry deposition could be estimated from the NTN network.

Supplying data for trends determinations was selected next because legislation authorizing NAPAP requires documenting spatial and temporal changes of acidic precipitation.

Based on the possible economic impact resulting from forest damage, terrestrial effects needs were then addressed. Timing of terrestrial effects research was also considered when ranking this user group. The forest research program will obtain data at three levels. Intensively managed research sites will generate data that will be used to direct chamber exposure programs. These intensive research sites will not be completely established until FY-87. The chamber studies will determine at what levels and on what temporal scale damage can be expected. This information will be verified by wide area routine monitoring. These monitors will not be required for 2-3 years. However, earlier deployment would be useful in beginning to establish a data base in the southern commercial forests.

The schedule for site deployment is shown in the following chart:

	1986		1987		1988	
	January	July	January	July	January	July
Model Evaluation Northeast	3 sites	. . .	. 27 sites			
Forest Effects Southeast		5 sites				
Sensitive Eco-Systems West					10 sites	

The monitoring needs in the western United States was selected as the final topic addressed by the group. This area was chosen for routine monitoring consideration because of existing research programs

in the west and the potential effect of dry deposition on the natural ecosystems.

From a geographical perspective the priority ranking of the user groups also allowed several regions of the country to receive coverage. The model evaluations encompass the northeastern states, the terrestrial effects research covers primarily the Southeast, and the sensitive systems are being studied in the West.

C. Siting Strategies

1. Model Evaluation

In performing a model evaluation, the output fields of the model will be compared with observations in the northeastern United States. Output fields of major interest are regional patterns of deposition for sulfate, nitrate and hydrogen ion and patterns of ambient air concentrations of SO_2 and O_3. For dry deposition the comparison will need to be indirect, since dry deposition is generally inferred from near-surface ambient air measurements using appropriate deposition velocities to obtain dry deposition fluxes. Thus the evaluation of dry deposition will stress the comparison of predicted ambient concentration fields against observations.

It is necessary, therefore, that the monitoring network be capable of identifying the major features of deposition and air concentrations in the Northeast for comparison with model predictions. These features are the peaks (magnitude and location), the gradients away from the peaks, and the magnitude of the wings of the regional pattern. These features need to be identified for time scales as short as an event and as long as an annual average. Data and model outputs indicate that the steeper gradients occur over distances of 150 km for events and over distances of 300 km for seasons. Also the ratio of the peak to the wings of the patterns is generally not large, seldom greater than a factor of two. Site spacing within networks will need to be on a scale that is similar to (or smaller than) the major features to reliably identify them.

NADP/NTN wet deposition data and air concentration data obtained in the Northeast (by the SURE program) show evidence of random variations superimposed on the large-scale deposition and air concentration patterns. The implication is that monitoring sites are probably not regionally representative, i.e., not always equal to deposition or concentrations averaged over areas 100 x 100 kms. Model predictions, on the other hand, are assigned to regional scale areas because of the use of large grid cells (80 km or more on a side). Thus, a model evaluation should use spatial patterns estimated from observational data as a basis of comparison rather than individual site values.

For data versus model comparisons to be interpretable, the patterns should have commensurate spatial scales of averaging. This necessitates smoothing or filtering the observational data to a degree consistent with the model predictions. Because of other variations in observations, a smoothed spatial pattern estimated from them has a

component of uncertainty associated with it. In performing a model evaluation, it is important to account for the error in the estimated pattern.

A spatial pattern representing model output cannot be expected to conform precisely to that inferred from data. It should, however, lie within the uncertainty in the spatial pattern of the data. For the comparison between model and data patterns to be rigorous, the uncertainty in the spatial pattern must be within acceptable limits. If the uncertainty is too great, the evaluation will not be sensitive to a model's departure from reality. In designing the surface network, it is therefore essential to define criteria for acceptable limits of uncertainty in spatial patterns that can be estimated from the network. The following are operational criteria that provide a reasonable degree of sensitivity for model evaluation:

> The relative uncertainty in seasonal estimates from the network should not exceed about 60%. In the regions of highest deposition or concentration, relative uncertainty in estimates should not exceed 30%.

An interpolation method known as kriging can be used to evaluate the proposed surface network against these criteria on observed data. Kriging produces a "regression-like" smoothed estimate of the surface passing through spatial or geographic variables. It also produces an estimate of the uncertainty (expected squared error) of the interpolated points. Thus it can be used to place confidence bands about the estimated spatial patterns. This later feature makes kriging unique among interpolation schemes. The uncertainty estimates are then compared to the above criteria to determine the acceptability of the network design. Model output fields are used as a second design check or evaluation of the proposed surface network. The model output pattern for RADM is sampled at the network sites and a new pattern interpolated from this data. The two patterns are compared to check if the network can identify the major features originally in full model output.

The result of the design analyses is that the full first 30 sites of the NTN Dry Deposition Network are necessary for model evaluation purposes. In fact these stations must be augmented with 40 more stations to achieve the necessary spacing of stations in gradient areas and to achieve the design criteria. The proposed model evaluation surface network for the Northeast is composed, therefore, of the present 5 NTN dry deposition sites, the first 30 new NTN dry deposition sites, the present 17 UAPSP sites in the east which will become part of EPRI's OEN network, 3 new EPRI OEN sites, 4 stations from a new New York network and 11 stations from Canada, for a total of 70 stations. The design analysis has also shown that the number of Canadian sites needs to be increased.

2. Trends and Aquatic Effects

The data needs for both trends determination and aquatic effects

are similar. Both need general coverage of the study area. Thus the needs of both groups are for the network to be capable of identifying regional patterns of deposition for total sulfur (wet and dry) together with an uncertainty estimate about the pattern. The deposition at a particular site, with its uncertainty, is to be interpolated from the regional pattern. Preliminary estimates have indicated that the uncertainty be of the order of 50%, which is comparable to the needs of model evaluation. Hence, network needs for aquatics and trends overlap network needs for model evaluation in the Northeast. A similar spacing of stations is required for both. The gradients in the Southeast are much less than in the Northeast. Design work is necessary to establish the number of sites needed to establish a pattern with adequate uncertainty bounds in the Southeast.

3. Terrestrial Effects

Characterizing the exposure of terrestrial ecosystems to air pollution/ dry deposition is needed for several reasons. It is required (1) to provide design criteria for controlled exposure studies; (2) to provide deposition estimates for controlled exposure studies; and (3) to determine if effects observed in controlled studies are occurring in forests at the anticipated exposure levels.

The group recommends that five routine monitoring sites be located in the southern commercial forest cooperative research area. The strategy for locating these sites will take into consideration the planned location of the six intensive research sites and the three EPRI sites. Because of the generally small pollutant gradients throughout the research area, the eleven sites plus the three EPRI sites should be sufficient to describe actual exposure for the area. Additional design efforts will be undertaken to confirm this assumption. If additional sites are required, efforts will be made to have state (or local) agencies, and industry organizations provide needed monitoring resources.

4. Sensitive Region Effects

The working group discussed various strategies for selecting monitoring locations in the sensitive ecoregions of the West. As with any monitoring network designed to accomplish multiple objectives certain conflicts arise and priorities must be established.

The working group agreed that the primary objectives for western siting of dry deposition monitoring are to provide (a) data in support of existing research projects and (b) data to support the national assessment of acid deposition. Since there are currently no plans to apply RADM in this environment, the modeling evaluation needs for monitoring data are not a high priority in this region. Rather than arbitrarily locating one site per state, the working group developed a strategy based on: (a) existing source regions, (b) anticipated growth in the emissions inventory, (c) climatic/ecological considerations, (d) important receptors, and (e) the current inventory of western acidic deposition research locations.

The SO_2 emissions pattern in the West is dominated by smelters, power plants and assorted industrial facilities. Two general regions of significant emissions are southern Arizona and the Four Corners area (CO, UT, AZ, NM). NO_x emissions are dominated by urban areas, power plants and other industrial facilities. The existing emissions are strongest in California, Arizona, the Four Corners area and Colorado.

The SO_2 growth scenario is dominated by smelter control issues, especially associated with the Nacozari (Mexico) and Cananea smelters, 80 and 40 km southwest of the Arizona, New Mexico, Mexico boundary. These smelters emit 625,000 tons/year of SO_2, a major fraction of the entire western inventory. A second significant SO_2 emission growth area is associated with sour gas developments in southwestern Wyoming. NO_x emissions are projected to grow in the urban areas, southern California, central Arizona and central Colorado. Point source NO emissions are also associated with oil shale development in western Colorado.

The west can be roughly divided into five ecoregions, namely, desert, grass-shrub land, montane, sub-alpine and alpine in order of increasing precipitation and elevation and decreasing temperatures. For the simple reason that there is little precipitation, it is likely that dry deposition/wet deposition ratios are greatest in desert areas.

Of primary concern in the western United States are so-called Class I areas. These areas were established by the Clean Air Act (1977) as locations where no adverse impacts of new sources on the "air-quality-related-values" of the areas is allowed. Thus, decisions about the impacts of proposed sources on Class I receptors, primarily high elevation wilderness and national parks are operational components of western air quality managements.

Although there are numerous locations where research is being conducted, the working group focused its attention on active ecological and acidic deposition research sites. In particular, from the total population of such sites, locations were selected because of their long-term ecological research focus and their locations. Areas selected are:

San Dimas Experimental Forest

Sequoia National Park

H. J. Andrews Experimental Forest

Bend, Oregon vicinity - located to observe gradient in deposition from wet to dry in a basically clean air environment

Central Plains Experimental Range

Fox Park, Wyoming

Niwot Ridge/Fraser Experimental Forest

Pinedale, Wyoming

Molas Pass/Durango, Colorado Area - located to observe gradient associated with major sources

Navajo Reservation, Arizona Area - located to observe major source gradient

Southeastern Arizona Area - located near major SO_2 emission sources in an area anticipated to receive maximum SO_2 dry deposition

Sites for the western region will be located, where possible, to meet the needs of the trends network as well as the effects researchers.

D. Conclusions

The working group developed network strategies for dry deposition monitoring based on stated priorities, scientific need, and available resources. Adoption of the group report by NAPAP and its member agencies is essential for future planning purposes. It is imperative that researchers know the extent and magnitude of support that can be expected from a routine dry deposition monitoring network. Guidance from this report will also enable program managers to more effectively plan and manage their limited resources.

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